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13. ABSTRACT ***(Maximum 200 Words)***

In 1992, Congress allocated funds for development of expertise in applied environmental bioremediation restoration technology including work on process integration, scale-up and demonstration of the Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) process. Specific targets included the treatment of chlorinated solvents, nitrated compounds and aromatic hydrocarbons. The goal of this SERDP funded project was to conduct experimental work at the bench-scale through field demonstration using the GAC-FBR as the platform for degradation of these compounds of concern.

In this report are the results of a three-year program designed to test and demonstrate the GAC-DBR process for a number of problem wastewaters facing the U.S. Armed Forces. Both laboratory-pilot and field demonstrations using small commercial scale GAC-FBR systems were conducted.

14. SUBJECT TERMS

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AEROBIC GRANULAR ACTIVATED CARBON-FLUIDIZED BED REACTOR (GAC-FBR) TREATMENT OF A SYNTHETIC GROUNDWATER CONTAINING BTEX AND TCE

Final Report

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COMMON ABBREVIATIONS

BTEX	benzene, toluene, xylene
DO	dissolved oxygen
DCE	dichloroethylene
FBR	fluidized bed reactor
GAC	granular activated carbon
GAC-FBR	granular activated carbon-fluidized bed reactor
GC	gas chromatography
HRT	hydraulic retention time
TCE	trichloroethylene
VC	vinyl chloride
TSS	total suspended solids
VSS	volatile suspended solids

EXECUTIVE SUMMARY

This report details experimental results obtained using a laboratory-pilot scale aerobic granular activated carbon fluidized bed reactor (GAC-FBR) to treat a synthetic groundwater containing BTEX and TCE. Batch assays using biomass from the GAC-FBR were performed to determine the kinetics of TCE and anaerobic dechlorination by-products. The key results attained include:

- A GAC-FBR system, fed synthetic groundwater containing BTEX and TCE, was started-up under ambient temperature conditions (21-22°C). The synthetic groundwater contained 190 μg TCE/L and 6000 μg BTEX/L. The hydraulic retention time (HRT) was 5.9 minutes. A stable biofilm was formed on GAC carrier within 10 days; BTEX removal efficiency was greater than 99%. TCE in the influent did not inhibit the development of a biofilm or BTEX removal efficiency.
- Sustained, co-metabolic TCE degradation in the GAC-FBR was verified by changing the amount of oxygen delivered to the reactor influent. No TCE removal occurred when DO was not supplied. TCE removal capability was restored when oxygen was again added to the influent.
- Throughout this study, the reactor was loaded with the same mass ratio among benzene, toluene and xylene was 1:2:1 (wt/wt). TCE degradation performance by the GAC-FBR was examined at four different steady-state conditions under ambient temperature conditions (18-24°C) with one-pass feed at 5.6 minute HRT. Under all test conditions, with BTEX loading rates ranging from 1.9 to 4.6 Kg COD/m^3-d, BTEX removal efficiencies were greater than 99.9%. The effluent BTEX concentrations were, in general, below detection limits.
- Under the first steady-state condition, the reactor was fed a moderate TCE concentration (380 μg/L) with a BTEX/TCE loading ratio of 17/1 (mg/mg); average TCE removal efficiency was 32.7% with a BTEX/TCE consumption ratio of 44.9 mg/mg.
- The second steady-state condition was designed to test TCE removal performance with an increased BTEX/TCE loading ratio (37/1) and reduced TCE concentration (160 μg/L). An

average TCE removal efficiency of 30.8% was achieved; the BTEX/TCE consumption ratio was 110.9 mg/mg. The results indicated that the increased BTEX/TCE loading ratio did not improve TCE removal efficiency.

- The third steady-state condition was designed to test TCE removal performance at a reduced BTEX/TCE loading ratio (17/1). TCE concentration was held constant (180 μg/L), while BTEX concentrations were reduced. Average TCE removal efficiency was 36.3% at a BTEX/TCE consumption ratio of 41.8 mg/mg. This suggests that a lower BTEX/TCE ratio might increase TCE removal efficiency slightly.
- The fourth steady-state condition was designed to test TCE removal performance with a low influent TCE concentration (ca. 60 μg/L). The BTEX/TCE loading ratio was 50 mg/mg. An average TCE removal efficiency of 19.0% was achieved with a BTEX/TCE consumption ratio of 109 mg/mg.
- The results obtained from batch assays and reactor profile analyses indicated that co-metabolic TCE degradation rate was inhibited in the presence of BTEX. The batch assays indicated that the biomass taken from upper portion of the fluidized bed had sufficient TCE degradation capability when the BTEX/TCE and toluene/TCE consumption ratios were as low as 42 and 21 mg/mg, respectively. Co-metabolic TCE transformation could be described using first order kinetics for the range of TCE concentrations tested.
- The biomass from the GAC-FBR were capable of degrading TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, and vinyl chloride. The degradation rates for *cis*-1,2-DCE and VC, two major anaerobic metabolic intermediates of TCE, were almost three-fold of that for TCE with much less inhibition observed.
- Based on the results obtained from reactor operation and batch assays, TCE removal performance by the GAC-FBR with different HRT and influent TCE concentrations was estimated using kinetic analysis and modeling. High TCE removal efficiency can be expected at increased HRTs.
- High TCE removal efficiency (70%) was achieved with a longer HRT (26.9 minutes) and a TCE concentration of 48.3 μg/L when recirculation of reactor effluent was used. This confirmed modeling results.

1. OBJECTIVES AND STRATEGY

1.1 Background of this Project

Chlorinated hydrocarbons, such as perchloroethylene (PCE), trichloroethylene (TCE), have been used as solvents and degreasers in many processes. The EPA estimated that in 1974 approximately 310,200 tons of waste solvents were produced by degreasing operations (U.S. EPA, 1979). In contaminated aquifers, the most frequently observed chlorinated hydrocarbons are TCE and related anaerobically dechlorinated intermediates such as dichloroethylenes (DCEs) and vinyl chloride (VC). These compounds are known or suspected carcinogens. Cost-effective and timely technologies are not yet available for clean-up of groundwater contaminated with TCE and its dechlorination intermediates.

It has been observed that TCE and other chloroaliphatics can be degraded to CO_2, H_2O and chloride ions by a variety of aerobic bacteria which contain broad-substrate-specificity oxygenases. Bacteria possessing this ability include toluene-oxidizing bacteria (Nelson et al., 1987; Wackett, et al., 1988), methane oxidizing bacteria (Wilson and Wilson, 1985; Fogel et al., 1986; Henson et al., 1988; Little et al., 1988; Tsien et al., 1989; Hanson et al., 1990; Oldenhuis et al., 1991), ammonia-oxidizing bacteria (Arciero et al., 1989; Rasche et al. , 1990a, 1990b; Vannelli et al., 1990), propane-oxidizing bacteria (Wackett et al., 1989), and propylene-degrading bacteria (Ensign et al., 1992). The enzymes which have been implicated in catalyzing TCE oxidations are toluene mono- and dioxygenase (Winter et al., 1989), soluble methane monooxygenase (Wilson and Wilson, 1985; Fogel et al., 1986; Henson et al., 1988; Little et al., 1988), ammonia monooxygenase (Arciero et al., 1989; Rasche et al., 1990; Hyman et al., 1995), propane monooxygenase (Wackett et al., 1989), and alkene monooxygenase (Ensign et al., 1992). When these bacteria are grown on methane, toluene, propane, or isopropylbenzene as energy sources, they co-incidentally oxidize TCE and other chloroaliphatics. Microorganisms known to degrade TCE via aerobic co-metabolism include:

- Methanotrophs including *Methylosinus trichosporium* OB3b (Oldenhuis et al., 1989; Tsien et al., 1989), *Methylococcus capsulatus* (Green and Dalton, 1989) and other species (DiSpitito et al., 1992; Tsien and Hanson 1992);

- Pseudomonad which degrade toluene and phenol as well as benzene including *Pseudomonas mendocina* KR1 (Winter et al. 1989), *Pseudomonas putida* F1 (Wackett and Gibson, 1988), *Burkeholderia cepacia* G4 (Shields et al., 1989; Folsom et al., 1990), *Pseudomonas pickettii* PKO1 (Kukor and Olsen, 1990), and *Pseudomonas fluorescens* PFL12 (Vandenbergh and Kunka, 1988);
- Propane-degraders including *Mycobacterium vaccae* JOB5, *Mycobacterium convolutum*, *Mycobacterium rhodochrous* W-21, W-24 and W-25 (Wackett et al., 1989);
- Ammonia-oxidizing *Nitrosomonas europaea* (Arciero et al., 1989); and
- Alkene-degrading *Xanthobacter* sp. (Ensign et al., 1992), *Alcaligenes denitrificans* subsp. *xylooxidans* JE75, and *Rhodococcus erthyropolis* JE77 (Ewers et al., 1990).

In the early 1990s, most research work focused on examining the applicability of methanotrophic TCE degradation. Methanotrophic species, especially type II, contain predominantly soluble methane monooxygenase (sMMO) when grown under copper limited conditions. When methanotrophs are grown on copper-rich media, they synthesize particle monooxygenase (pMMO) which degrades TCE poorly (DiSpirito et al., 1992). Pure and mixed methanotrophic cultures grown on copper limited media showed rapid initial TCE degradation rates (Alvarez-Cohen and McCarty, 1991a, 1991b; Henry and Grbic-Galic, 1991a, 1991b; Oldenhuis et al., 1991). Although sMMO degrades TCE rapidly, it is difficult to achieve stable TCE degradation performance in continuously fed reactor systems during long-term reactor operation. This is because sMMO is inactivated during TCE degradation and the growth of methanotrophs is inhibited in the presence of TCE (Alvarez-Cohen and McCarty, 1991; Henry and Grbic-Galic, 1991; Oldenhuis et al., 1991). In addition to the inactivation by TCE, the presence of copper in the water being treated may force methanotrophs to synthesize pMMO or result in a change in the methanotrophic population from sMMO-producing species to predominantly pMMO-producing species, resulting in loss of TCE transformation capacity even though methane may still be consumed at high rates.

Studies using several pure Pseudomonad cultures indicated that those species utilize aromatic compounds such as toluene or phenols are capable of co-metabolically degrading TCE

via toluene mono- and dioxygenases. Co-metabolic TCE oxidation by these organisms is also associated with enzyme inactivation (Wackett and Householder, 1989), resulting in a rapid loss of TCE degradation activity. Interestingly, it was reported recently that TCE-degrading activity (toluene dioxygenase) in several Pseudomonad was induced by TCE, *cis*-1,2-DCE, PCE, and chloroethane (Heald and Jenkins, 1994; McClay et al., 1995). This indicates that the presence of TCE is , at least, not inhibitory for the growth of the organisms capable of co-metabolizing of TCE. The oxidation of toluene (or phenol) and TCE degradation are competitive reactions because both reactions are performed by the same enzymatic system (Folsom and Chapman, 1991; Folsom et al., 1990; Landa et al., 1994). Degradation of TCE in the presence of the primary substrate is greatly reduced.

Methanotrophic bacteria are capable of co-metabolism of TCE and have been used for TCE degradation in batch tests and continuous-feed reactors (Jewell et al., 1990; Hicks et al., 1991; Hsueh et al., 1991; Phelps et al., 1990; Strand et al., 1991). Reactor tests using phenol as the primary substrate (Ensley and Kurisko, 1994; Folsom and Chapman, 1991; Coyle, et al. 1993; Hecht et al., 1995; Segar et al., 1995), toluene (Landa et al., 1994) have also been conducted. Most of these studies were small scale used for feasibility study and kinetic analysis.

The aerobic granular activated carbon fluidized bed reactor (GAC-FBR) has been developed for improved biodegradation of volatile hydrocarbons including BTEX (benzene, toluene, xylenes). Past experience demonstrates that BTEX can be efficiently degraded to CO_2 in the GAC-FBR system (Hickey et al., 1991). We have also successfully tested TCE degradation using methanotrophic bacteria in the GAC-FBR during the past five years (Wu, et al., 1993). Since TCE and less-chlorinated ethylenes (DCEs and vinyl chloride) are frequently found together with BTEX at many contaminated sites, it is of significance to develop a treatment process capable of degrading these contaminants simultaneously. In this study, we used the GAC-FBR to treat a synthetic groundwater containing BTEX and TCE as contaminants to demonstrate that TCE can be removed in the reactor via co-metabolism. The results obtained from this study can be used for reactor scale-up and field pilot-tests.

1.2 Objectives of this Study

The primary focus of this study is to investigate the treatment of trichloroethylene (TCE) in the presence of benzene, toluene, ethylbenzene and xylene (BTEX) as co-contaminants (or co-substrates) using the GAC-FBR system. This study is designed to treat TCE based on the fact that toluene-degrading aerobic bacteria can degrade TCE via co-metabolism and BTEX are common contaminants often observed together with TCE and other chlorinated hydrocarbons in groundwater. Feasibility of the treatment will be assessed by:

- Biological start-up of GAC-FBR in the presence of both TCE and BTEX,
- Evidence of co-metabolic TCE degradation in GAC-FBR,
- BTEX removal efficiencies and rates,
- TCE removal efficiencies and rates,
- Mass ratio of BTEX/TCE consumption,
- Influence of BTEX on TCE degradation,
- Kinetics of TCE degradation by biomass from the GAC-FBR, and
- Biodegradation of other chlorinated ethylenes by biomass from the GAC-FBR system.

1.3 Experiments Conducted

The experiments conducted were separated into five tasks that address one or more of the areas listed above. The specific tasks are:

Task 1: Start-up of a laboratory GAC-FBR system using synthetic groundwater.
Task 2: TCE degradation performance with different TCE and BTEX concentrations in the influent with one-pass feed (i.e. no recirculation).
Task 3: TCE degradation performance with different TCE and BTEX concentrations in the influent with recirculation.
Task 4: Characterization of the system biomass for TCE degradation kinetics and biodegradation capabilities.
Task 5: Kinetic analysis and modeling for estimation of TCE removal performance.

The experimental matrix for the reactor testing (Tasks 1, 2 and 3) is summarized in Table 1-1. All tests were performed using a typical 10-liter laboratory-scale GAC-FBR system operated at ambient temperature conditions (18-24°C). In Task 2, two BTEX/TCE mass loading ratios were used in order to study the influence of BTEX/TCE loading ratio or BTEX/TCE consumption ratio on TCE degradation performance. The hydraulic retention time was ca. 5.9 min in the fluidized bed. The Task 3 work was designed to test the effect of increased HRT and recirculation on TCE removal efficiency in the same reactor. Task 4 work was performed using batch assays to determine TCE degradation kinetics and biodegradation capability of the biomass from the GAC-FBR (Table 1-2). Task 5 work was performed based on the results obtained from Tasks 1-4 to estimate TCE degradation performance of the GAC-FBR under different conditions.

Table 1-1. Experimental matrix design for testing TCE co-metabolic transformation capability of the GAC-FBR process using BTEX as the primary substrates.

		Influent		Influent Mass Ratio			
Days of Operation	**Task**	**TCE (μg/L)**	**BTEX (μg/L)**	**BTEX/TCE (μg/μg)**	**Toluene/TCE (μg/μg)**	**Flow Pattern**	**HRT (min)**
1-9	1	190	6000	32	16	One pass	5.9
10-95	2	380	6000	17	8.5	One pass	5.9
96-137	2	160	6000	37	18	One pass	5.6
138-158	2	180	3000	17	8.5	One pass	5.6
159-182	2	62	3000	50	25	One pass	5.6
183-233	3	48	8300	173	86	Recirculation	26.9

Table 1-2. Batch experiments conducted for characterization of kinetic capabilities of biomass from the GAC-FBR.

No.	Test	Test Method	Objectives
1	TCE degradation with and without BTEX	Headspace-free	Effect of BTEX on TCE degradation
2.	TCE degradation with different initial TCE concentrations	Headspace-free	TCE kinetics
3.	Degradation of TCE, *cis*-DCE, 1,1-DCE *trans*-DCE and VC	Headspace	Biodegradation potential

2. MATERIALS AND METHODS

2.1 *Granular Activated Carbon Fluidized Bed Reactor System*

The granular activated carbon fluidized bed reactor (GAC-FBR) system used for this work effort is illustrated in Figure 2-1. This reactor system included a reactor, feed mixing reservoir, effluent recycle reservoir, nutrient solution delivery system, oxygenated water delivery system, BTEX-TCE delivery system and related pumps. All components in contact areas were glass, Teflon and stainless steel. This reactor was operated at the standard conditions listed in Table 2-1. The reactor had seven sampling ports installed along reactor height to allow sampling for profiles of TCE, BTEX and DO through the reactor. The volume of the fluidized bed region (or biological reaction region) was 7 liters. Total reactor volume (including liquid-solid separation zone and effluent recycle reservoir) was 12 liters. In this report, the performance of the GAC-FBR is evaluated on the basis of the volume of the fluidized bed region (7 liters) rather than the total volume of reactor system because the ratio between the volumes of fluidized bed and liquid-solid separation zone will be different (generally 90% or greater of the total volume) in full-scale system depending on the reactor configuration employed.

The oxygenated water, BTEX-TCE solution, and inorganic nutrient solution were mixed together in the feed mixing reservoir just before they entered the reactor base. The feed mixing reservoir and effluent recycle reservoir were connected in parallel to the suction side of the fluidized pump. Because water is delivered under pressure to the influent reservoir, the fluidization pump draws exclusively from this reservoir when feed water pumping rate (a total flow rate of oxygenated water, BTEX-TCE solution, and nutrient solution) exceeds the fluidization pumping rate. The fluidization pump will draw effluent from the recycle reservoir only when the feed water pumping rate drops below fluidization pumping rate. Recirculation rate can be adjusted according to experimental requirements. A fluidization rate of 1.2 liters/min (15.7 gpm/ft^2) was used to obtain complete fluidization of granular activated carbon in this study. The initial fluidization of clean GAC was 50%. About 100% bed expansion was obtained when a mature biofilm became established on the GAC.

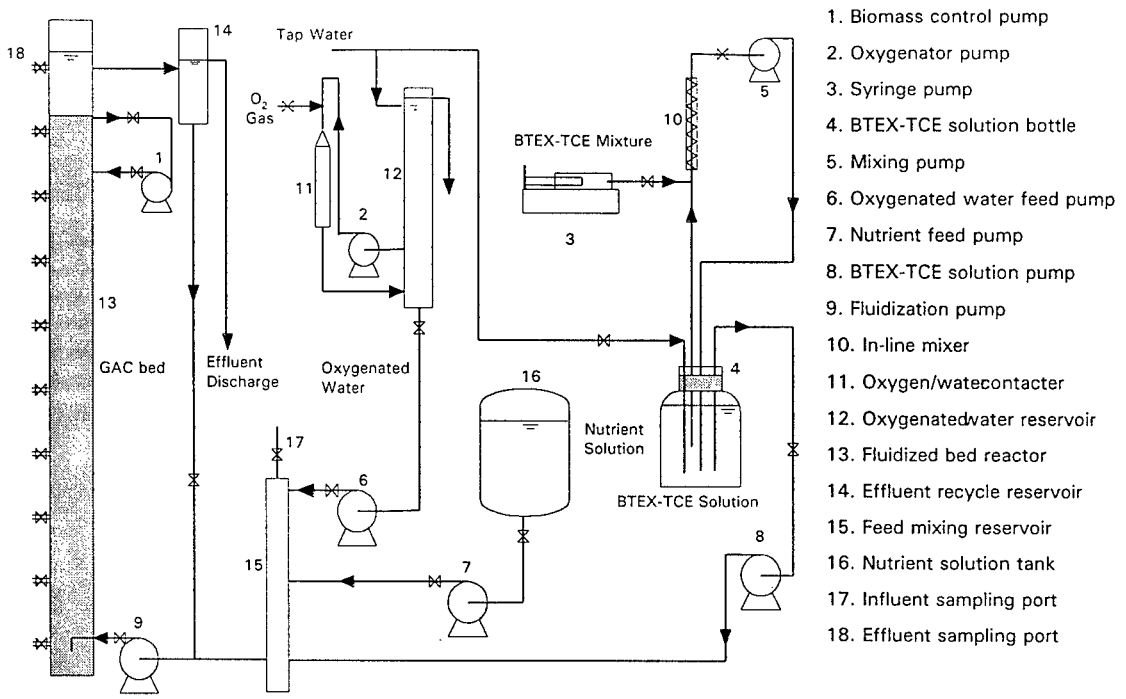

Figure 2-1. Schematic diagram of a GAC-FBR system for aerobic co-metabolic degradation of TCE with BTEX.

A media shearing pump located near the top of the reactor (Figure 2-1) was used to shear excess biomass from the GAC media and consequently control biofilm thickness and bed height. Less thickly coated (denser) GAC particles descend through the bed while the sheared biomass exits with the effluent.

Make-up water for the reactors was industrial grade tap water. Oxygenated water was prepared by recirculating make-up water through a downflow oxygen gas-water contactor and reservoir system. The oxygenated water delivery system can generate up to 45 mg/L DO in solution at the 1.2 L/min feed rate and temperatures of 16-20°C. The DO concentration in the oxygenated water can be adjusted by changing oxygen gas flow delivered to oxygen-water contactor.

Table 2-1. Standard operating conditions for GAC-FBR.

Hydraulic characteristics	
fluidized bed volume (liter)	7.0
solid-liquid separation zone (liter)	2.0
recycle reservoir (liter)	3.0
height (m)	3.0
volumetric upflow rate (L/min)	1.3
hydraulic loading rate (gpm/ft^2)	15.7
hydraulic retention time* (min)	5.6
GAC bed	
carbon	Calgon type MRX-P
size	10 X 30 mesh
initial charge mass (g)	1570
settled volume (L)	3.6
settled height (cm)	146
initial fluidization (%)	50
mixing fluidized bed height (cm)	294
*Based on fluidized bed volume (empty bed)	

The BTEX-TCE solution delivery system has five parts: a syringe pump to slowly meter in a BTEX-TCE solvent mixture; a recirculating pump to mix the reservoir bottle and carry the BTEX-TCE mixture into the bottle; a reservoir bottle (a 10 liter glass bottle) to provide enough time (retention time of 50 minutes or longer) for complete dissolution of BTEX and TCE; a stir plate to provide complete mixing in the reservoir bottle; and a BTEX-TCE solution diaphragm feed pump to deliver the BTEX-TCE solution from the reservoir bottle into the reactor. This system provides a stream of relatively constant concentration of BTEX and TCE for mixing with oxygenated water and nutrient solution. Note that slight variations in the flow of any of these three streams will result in some variability in both the TCE and BTEX concentrations. Because tubing pumps were used to provide the oxygenated water and nutrient solutions, there was some variation in the measured TCE and BTEX concentrations.

A nutrient solution was used to provide nitrogen and phosphorus for microbial growth. This solution was prepared in a 50 gallon plastic drum and fed to the reactor via a nutrient feed pump at a constant rate of 150 ml/hr. The chemical composition of the nutrient solution is presented in Table 2-2.

Table 2-2. Chemical composition of nutrient solution.

Chemical	Concentration (mg/L)
NH_4NO_3	766
K_2HPO_4	142
KH_2PO_4	278
Urea	586

In this study, oxygenated water, BTEX-TCE solution and inorganic nutrient solution were supplied to the feed mixing reservoir at rates of ca. 1000, 200 and 2.8 (mL/min), respectively, for Tasks 1 and 2. The oxygenated water and BTEX/TCE feed was reduced to 180 and 80 mL/min, respectively, for Task 3. For all cases, a COD:N:P ratio of 100:5:1 was maintained. The pH of reactor influent varied from about 7.8 to 8.5, depending on the pH of make-up water. The effluent pH varied from 6.2-6.8.

2.2 Sampling during Reactor Operation

The sampling locations for reactor influent and effluent are illustrated in Figure 2-1. Duplicate samples (10 ml) for analysis of BTEX and TCE were withdrawn from the reactor using a 20-ml glass syringe and gently dispensed into 22-ml glass vials through 3 inch, 15 gauge needles. The glass vials contained two drops of 10N NaOH for preservation and 2 grams of granular NaCl for enhancement of recovery of TCE during headspace GC analysis. The vials were sealed with Teflon coated septa and aluminum crimps. Samples were logged on a sample log form and usually analyzed on the same day. If not, they were immediately stored at 4°C for a total of 72 hours or less before analysis.

For each sampling location, a dedicated all-glass syringe was used. Syringes were rinsed with deionized water between uses and pre-rinsed with sample prior to withdrawal of the 20 ml sample volume for analysis. Reused vials were detergent and water washed, triple rinsed in deionized water and dried at 105°C for at least 24 hours. Septa were not reused.

The samples for DO and pH were analyzed immediately. The sampling procedure is described in Section 2.10.

2.3 Concentration Profiles through the GAC-FBR

The concentration profiles of compounds of interest (DO, BTEX and TCE) were monitored along the length (profile) of the FBR system. Samples were withdrawn from the sampling ports using a 20-ml glass syringe (headspace-free) and then injected into a 20-ml headspace vials (with 5 drops of 10N NaOH added) for BTEX and TCE analysis. Samples were taken beginning at the top of the bed and working down to prevent disruption of any concentration gradients due to sampling. The DO concentration was determined directly by lowering a YSI DO probe into the reactor.

2.4 Preparation of Stock Solutions for Batch Assays

The preparation of saturated stock solutions of TCE, *cis*-1,2-DCE, *trans*-1,2-DCE, and 1,1-DCE was performed by adding approximately 1.0 ml of respective solvent into a 160-ml serum bottle containing 10 glass beads and 100 ml of distilled water. The bottles were sealed with a Teflon-lined rubber septum and aluminum crimp-top cap, vigorously shaken by hand for three minutes to completely dissolve the solvents in water. Vials were then stored under ambient temperature conditions for at least overnight. At 20°C, a saturated stock solution contained approximately TCE of 1100 mg/L, *cis*-1,2-DCE of 3500 mg/L, *trans*-1,2-DCE of 6300 mg/L, or 1,1-DCE of 4000 mg/L.

2.5 Preparation of Cell Suspension for Batch Assays

The biomass used for the batch assays was obtained from an operating GAC-FBR. The collected biomass was dispersed into a homogenous cell suspension by repeatedly passing it through a 20-ml syringe equipped with a 24 gauge needle and stirring with a magnetic bar in a glass beaker. A phosphate buffer solution (pH 7.0, 3.0 M PO_4) was added to the cell suspension. The cell suspension used for the assays contained biomass concentrations of 0.8-1.3 gVSS/L. Biomass assays were conducted within one hour after collection of the sample. For abiotic controls, a portion of the cell suspension was autoclaved at 121°C for 30 minutes.

2.6 *Headspace-free Biodegradation Assays*

The headspace-free biodegradation assays were conducted in 100-ml batch reactors which were composed of a 100 ml glass syringe and a magnetic mixing bar driven by a magnetic mixer. Assays were conducted under ambient temperature conditions (20-23°C). The reactor is illustrated in Figure 2-2. The assays were performed in the absence and presence of BTEX in order to examine the effect of the presence of BTEX on TCE degradation kinetics. First, the cell suspension (10 ml) was injected into each syringe. Oxygenated water (containing approximately 20 mg DO/L) was then added bringing the total liquid volume to 100 ml. For the TCE degradation assays in the presence of BTEX, oxygenated water containing BTEX was used. Microliter amounts of a TCE aqueous solution (TCE concentration of approximately 1100 mg/L) were injected into the syringe reactor to achieve the desired initial TCE concentration. After mixing for one minute, liquid samples were withdrawn from the reactor (time zero) and added into duplicate GC headspace vials (5.0 ml for each vial). Prior to addition of the sample, each vial received 5.0 ml of distilled water, 2 grams of NaCl, and 0.08 ml of concentrated phosphoric acid. The vials were then sealed with a Teflon-lined rubber septum and aluminum crimps, ready for GC analysis. Liquid samples were then taken periodically according to a predetermined test schedule. The samples were analyzed within 24 hours.

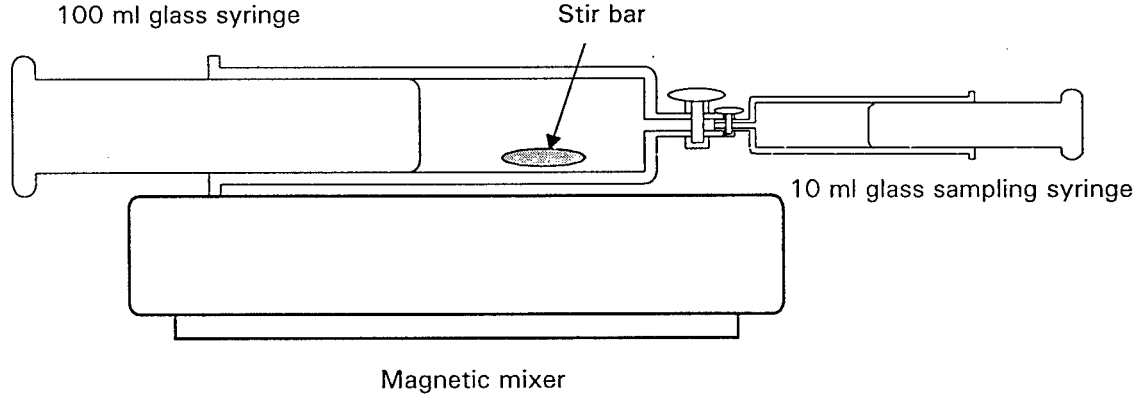

Figure 2-2. Bench scale, headspace-free reactor used for biodegradation assays.

2.7 *Biodegradation Assays with Headspace*

This biodegradation assay method was performed by analyzing gas composition in the headspace of test vials; this is similar to that reported by Alvarez-Cohen and McCarty (1991). Tests were performed in 65-ml vials sealed with Teflon-lined screw caps equipped with Mininert valves (Figure 2-3). Degradation of vinyl chloride was performed in 65-ml test vials sealed with a butyl rubber septum and screw caps. For all assays, 30 ml of a diluted cell suspension was added to each vial. After inoculation, the vials were sealed. No cell suspension was added to the control vials. For the TCE and DCE tests, the chlorinated hydrocarbon-saturated solution was added by microsyringe through the Mininert valves. For degradation of VC, a VC-nitrogen gas mixture, containing 5500 ppm of VC, was added with a gas-tight syringe into the vials to achieve the desired starting VC concentration. The vials were vigorously shaken by hand for 30 sec before initial headspace samples for TCE, DCE or VC were taken. Afterwards, the vials were placed in a 200 rpm shaker. Gas samples were withdrawn periodically with a 1000-µl Precision-lok, gas-tight syringe equipped with a 22-gauge side-port needle. The degradation rates for respective chlorinated ethylenes were determined from the changes in total mass of TCE, DCE or VC (including in both the liquid and gas phases), divided by the total biomass concentration (gVSS/L). The total transformation capacities for the respective chlorinated ethylenes were calculated based on the total mass of chlorinated hydrocarbon transformed, divided by the total biomass (as gVSS).

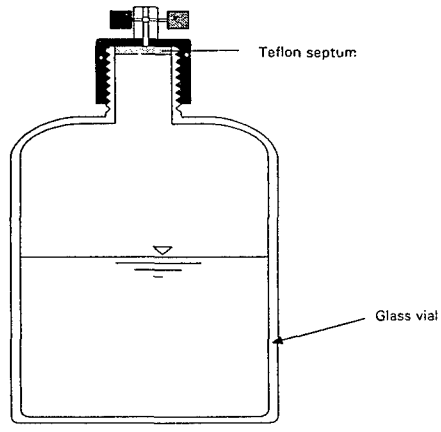

Figure 2-3. Vial sealed with a Mininert Teflon-lined screw cap equipped with a Mininert valve used for biodegradation assay.

2.8 Analysis of BTEX and TCE in Liquid Samples

BTEX and TCE were analyzed directly from the sample vials with a Tekmar Headspace Sampler attached to a Varian 3600 GC. Separation was accomplished with a Supelco, Inc. VOCOL column (30 m, 530 μm ID, 3.0 μm film). Detection was by flame ionization detector. GC conditions were: Injector - 250°C, Detector - 250°C, column 45°C for 5 minutes then ramped to 120°C at 20°C/minute. Headspace conditions were: sample loop 1.0 ml, loop temperature 150°C, constant hold time 1 hr at 80°C.

External calibration procedures were used for quantification. Five level calibration curves were prepared using stock solutions in methanol. Check standards were run with every sample batch and curves were updated if response varied more than ±10% from previous response. Retention times were updated with each standard injection. Reagent blanks were run in every batch to verify no sample contamination or carryover occurred from the headspace apparatus.

2.9 Analysis of Chlorinated Ethylenes in Gas Samples

During the headspace biodegradation assay, chlorinated ethylenes in gas samples were analyzed with a Hewlett-Packard 5890A GC equipped with a flame ionization detector (FID). Separation was performed by using a Carbopack B/1%SP-100 column (Supelco, Bellefonte, PA) at 180°C with helium as carrier. The injection volume was 100 μl. External calibration procedures were used for quantification.

2.10 Dissolved Oxygen (DO) and pH Measurement

Samples of effluent were collected in standard 60-ml BOD bottles. Three volumes of the samples were allowed to overflow the BOD bottle before capping. The samples of influent water were withdrawn using 60-ml polyethylene syringes to keep the samples headspace-free. The samples were analyzed immediately.

DO determination was made using a YSI-58 meter with a YSI 5730 stirring probe. Samples with DO less than 20 mg/L were determined directly. Samples with high DO (reactor influent and oxygenated water) were diluted with DO-free water to bring them into measuring range. Nitrogen purged water was prepared in 300-ml BOD bottles by purging with nitrogen gas. The background DO in a 300-ml BOD bottle was measured (generally 0.2-0.3 mg DO/L) using the DO meter. Subsequently, fifty ml of the DO-free water was withdrawn from the BOD bottle with a syringe, and fifty ml of the high DO sample was injected at the bottom of the BOD bottle. The DO probe was rapidly inserted into the bottle to measure DO concentration. The DO of the original samples was calculated based on the six-fold dilution taking into account the background DO concentration of the nitrogen purged water.

The pH was determined using a Chemcadet pH meter/controller (Cole Palmer Instrument Company, Chicago, IL) immediately after sampling using.

2.11 Chemicals

The chemicals used in this study were obtained from Aldrich Chemical Company, (Milwaukee, WI), Sigma Chemical Company (St. Louis, MO), or Malinckrodt, Inc. (Paris, KY). Vinyl chloride gas (5500 ppm in helium gas) was obtained from Matheson Gases & Equipment (Montgomeryville, PA). Oxygen gas was obtained from Union Carbide Corporation, Linde Division (Warren. MI).

3. REACTOR PERFORMANCE TESTS USING ONE-PASS FEED

The reactor was started-up on May 23, 1995 (day 0). From day 1 to day 182, the reactor was operated as a one-pass system (no-recirculation). The operational results during this period (Tasks 1 and 2) are summarized in Figures 3-1 through 3-8, including the changes in influent and effluent concentrations for DO (Figure 3-1), total BTEX (Figure 3-2), TCE (Figure 3-3), benzene (Figure 3-4), toluene (Figure 3-5), and xylene (Figure 3-6). The calculated results for TCE removal efficiency during the test period is presented in Figure 3-7.

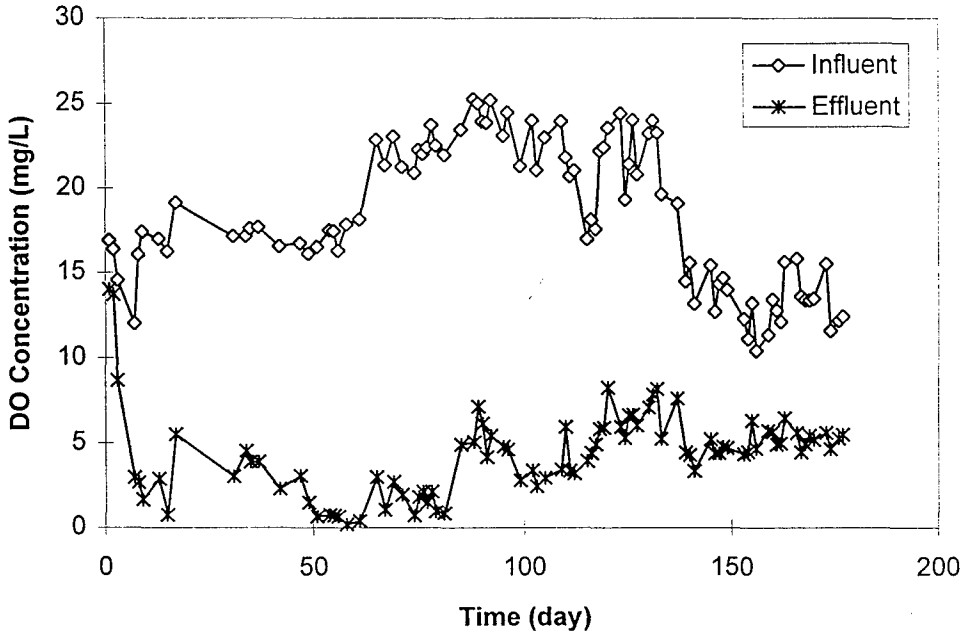

Figure 3-1. Dissolved oxygen concentrations in reactor influent and effluent during operational period with one-pass feed.

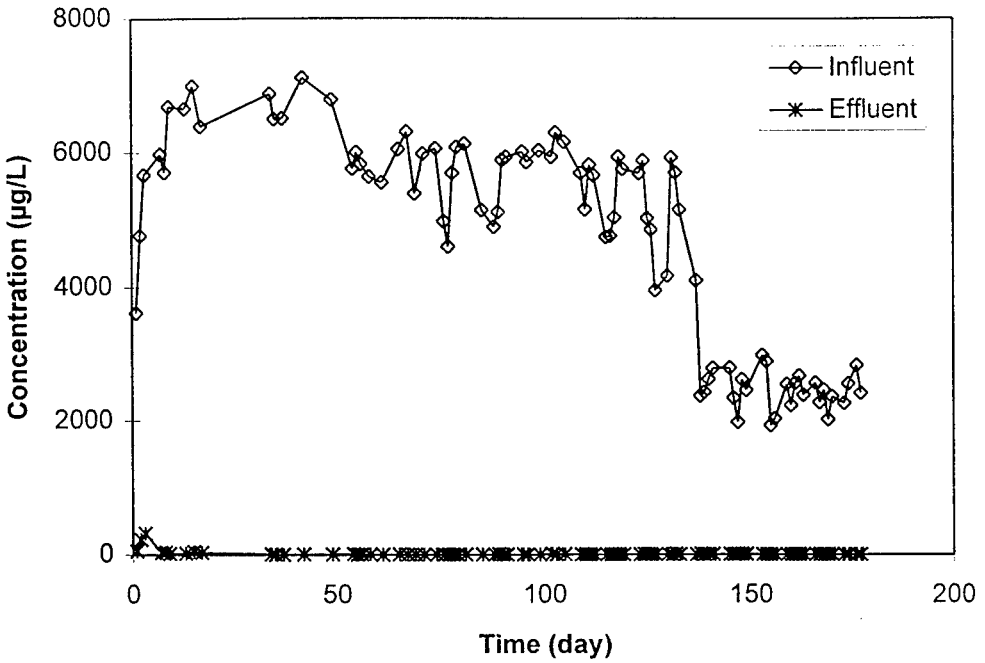

Figure 3-2. Total BTEX concentrations in reactor influent and effluent during operational period with one-pass feed.

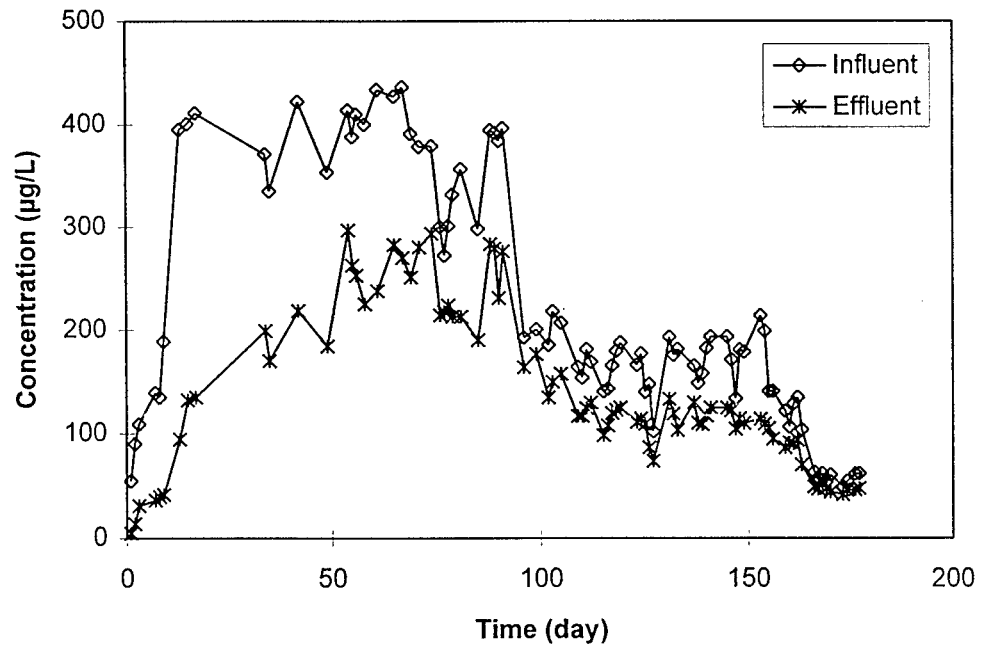

Figure 3-3. TCE concentrations in reactor influent and effluent during operational period with one-pass feed.

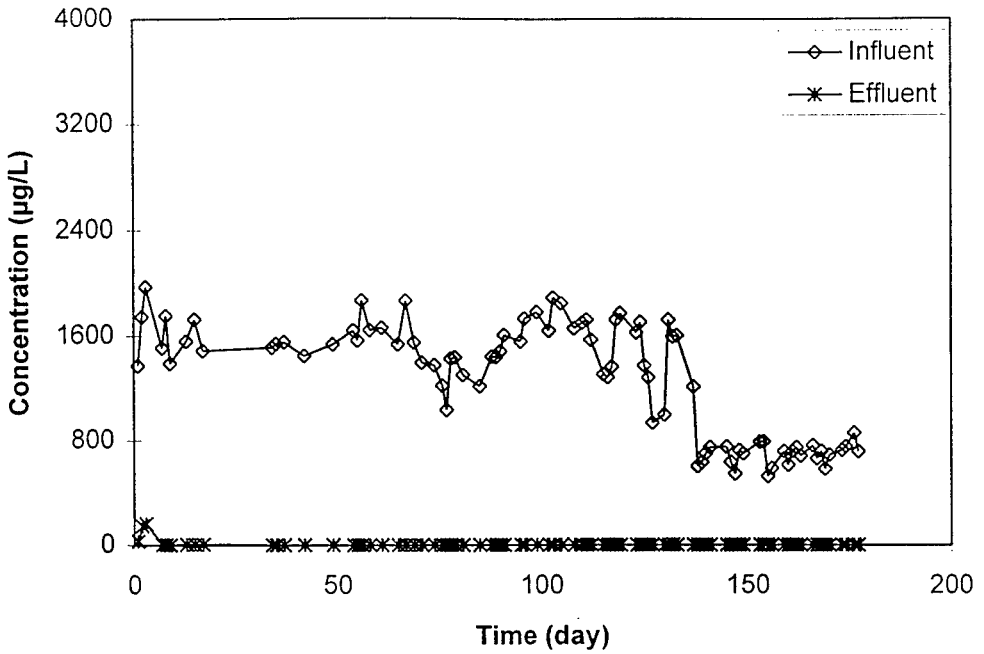

Figure 3-4. Benzene concentrations in reactor influent and effluent during operational period with one-pass feed.

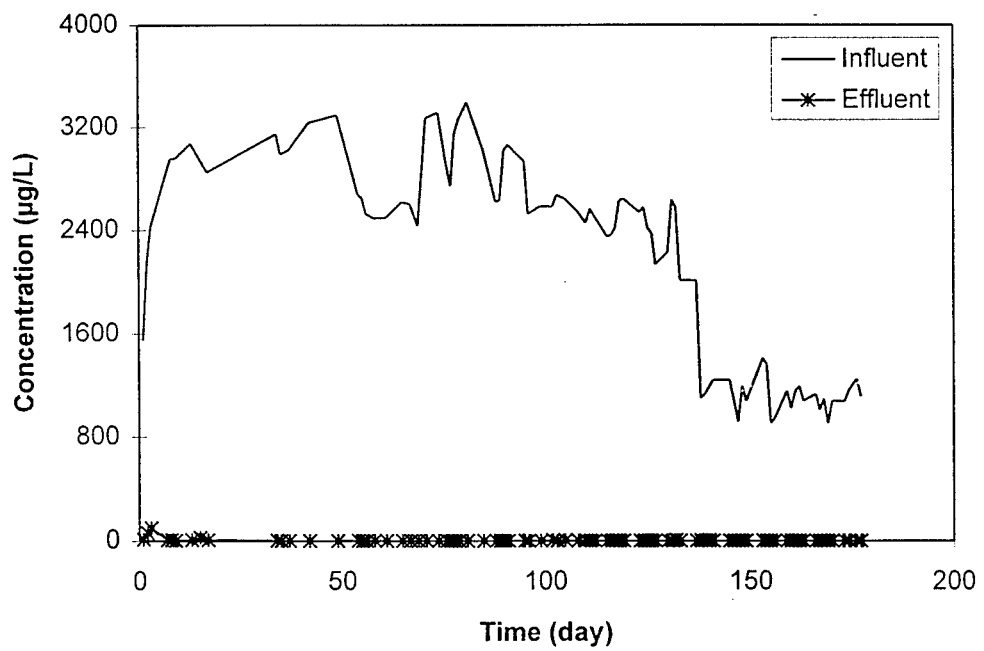

Figure 3-5. Toluene concentrations in reactor influent and effluent during operational period with one-pass feed.

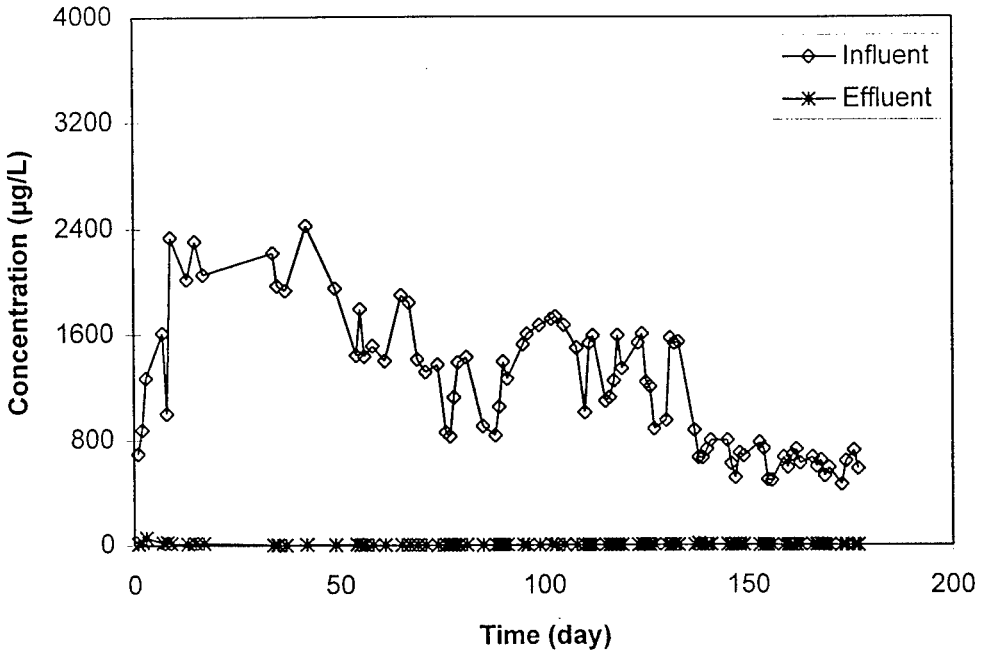

Figure 3-6. Xylene concentrations in reactor influent and effluent during operational period with one-pass feed.

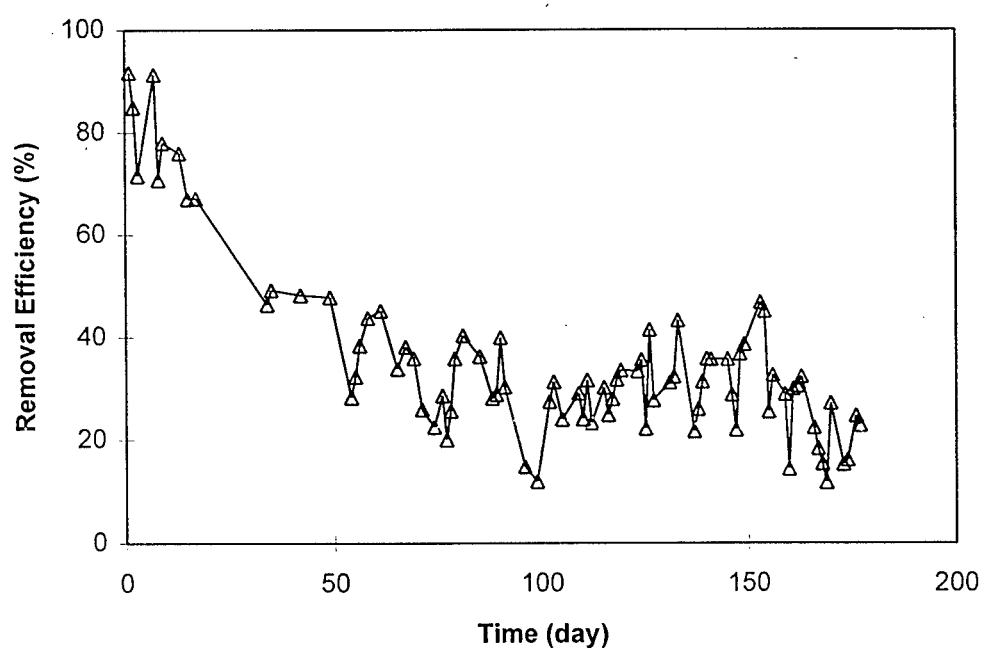

Figure 3-7. TCE removal efficiency during operational period with one-pass feed.

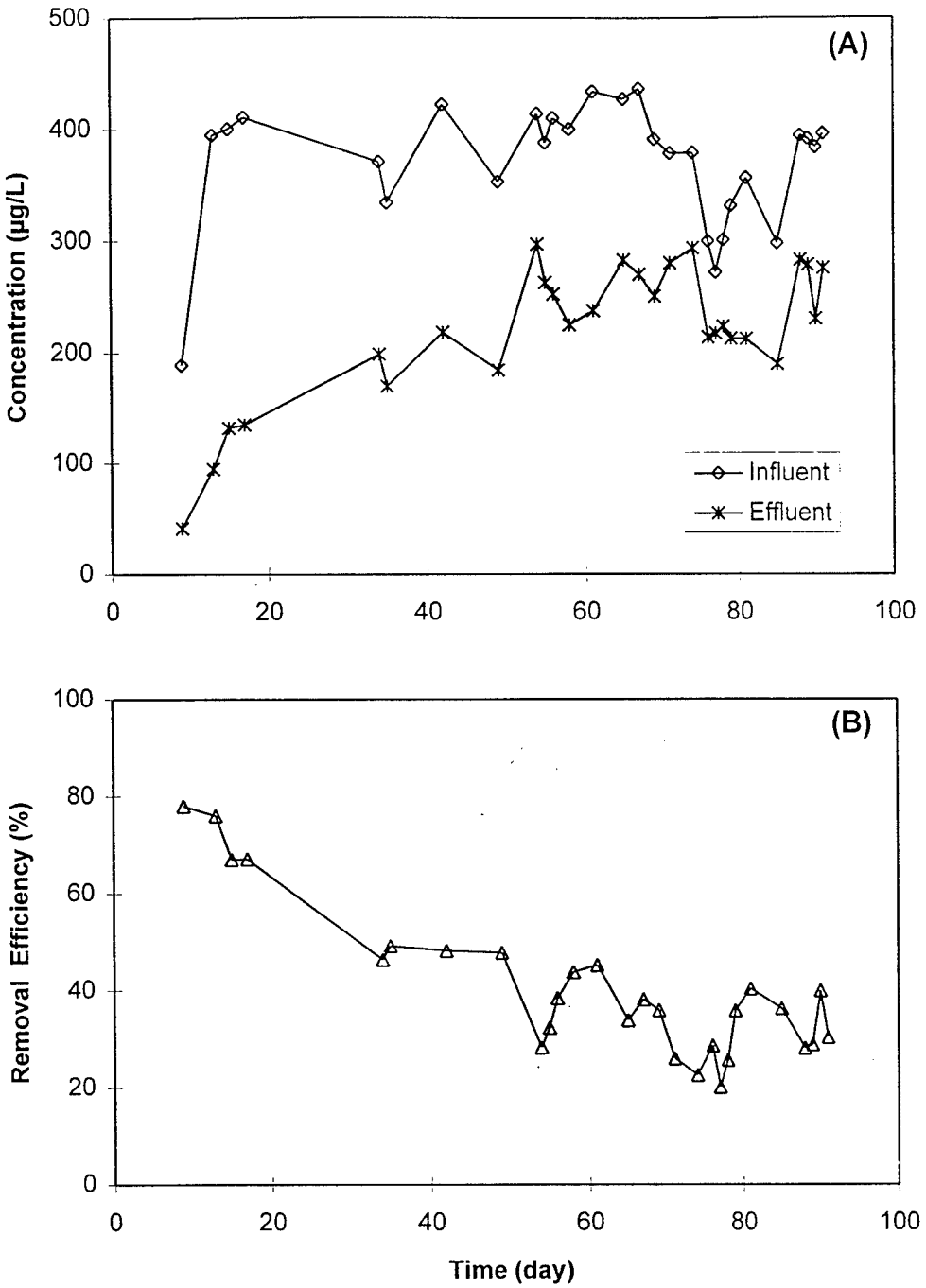

Figure 3-8. TCE concentrations in reactor influent and effluent (A) and TCE removal efficiency (B) during operational period I (days 9 to 95).

From day 183 to day 233, the reactor was operated with recirculation. This data is presented in Section 6.

3.1 Reactor Start-up

The reactor was inoculated with 2 liters of biofilm coated GAC media from a GAC-FBR which was used for the treatment of BTEX-contaminated groundwater, and 200 ml of activated sludge obtained from East Lansing, MI, Wastewater Treatment Plant. Complete recycle was maintained for two hours to encourage microbial attachment. Influent flow was then started. The influent had approximately 6000 μg BTEX/L (with a ratio of benzene:toluene: xylene of 1:2:1) and 190 μg TCE/L.

After continuous feed for two hours, samples were taken for determination of DO and pH in influent and effluent. The influent pH was approximately 8.2 while effluent pH was about 7.0, suggesting that CO_2 was being produced. The difference between influent and effluent DO concentrations was 1.5 mg/L. This observation indicated that oxygen and BTEX consumption was occurring in the reactor.

The start-up of the reactor was rapid. Visible biofilm growth on the GAC was observed seven days after inoculation. Effluent BTEX and TCE concentrations were low (Figures 3-2 and 3-3). This removal was due, to a large extent, to adsorption by the GAC media. The difference between influent and effluent DO concentrations on day 1 was ca. 2.9 mg/L. DO consumption increased continuously over the next week (Figure 3-1), indicating biological activity was gradually increasing. By day 9, effluent benzene and toluene in the effluent were below detection limits (<0.2 μg/L). Effluent xylene concentrations were just above detection limits (>2 μg/L). By day 9, DO consumption reached 16 mg/L with the ratio of DO consumption to BTEX removed of 2.6 mg/mg. This demonstrated that BTEX removal at this time was due to microbial activity. During this period, the height of the fluidized bed expanded due to the growth of biofilm on the GAC particles. The bed height increased from the initial height of 178 cm on day 1 to the control point (294 cm) on day 9. During the start-up period, TCE removal was high (>90% as shown in Figure 3-7), due to both biological transformation and GAC adsorption.

These results indicated that a fluidized bed reactor can be started-up rapidly using BTEX as primary substrate in the presence of TCE. TCE at 190 μg/L did not inhibit the development of biofilm on the GAC media.

3.2 Reactor Performance under Steady-state Conditions

After a stable biofilm was established (height of fluidized bed reached the control point), the reactor was continuously fed with BTEX and TCE using one-pass feed (no effluent recirculation). The ratio among benzene, toluene and xylene was fixed at 1:2:1 on a mass basis. The hydraulic retention time (HRT) in the fluidized bed reaction area was set at approximately 5.6 minutes. Four different combinations of influent TCE and BTEX concentrations were used in order to examine the influence of BTEX/TCE loading ratio and TCE concentration on TCE removal performance. Operational results under the four different steady-state conditions are presented in Table 3-1. Results for each experimental period are discussed in detail below as are results of experiments conducted to verify TCE removal was due to biological oxidation.

3.2.1 Verification of Biological TCE Removal

It is essential to verify when TCE transformation was attributed to co-metabolic degradation by microorganisms rather than carbon adsorption. The verification tests of biological TCE removal were performed twice. These were conducted by stopping the feed of oxygenated water on days 83 and 119. By these points in time, we estimated that, based on consistent removal efficiency, adsorption of TCE onto the GAC had essentially reached equilibrium.

Table 3-1. GAC-FBR system performance at steady-state conditions during one-pass operation.

Period	I	II	III	IV
Days	**85-92**	**117-137**	**146-154**	**168-177**
Operational Conditions				
Temperature (°C)	24.0±0.3	21.2±0.4	20.1±0.7	17.9±1.0
HRT (min)	5.9±0.1	5.6±0.12	5.6±0.1	5.7±0.1
pH				
influent	8.3±0.3	8.2±0.4	8.4±0.2	8.3±0.3
effluent	6.1±0.1	6.3±0.2	6.4±0.2	6.5±0.1
DO concentration (mg/L)				
influent	24.5±0.3	21.8±0.2	13.2±1.4	13.1±1.3
effluent	5.4±1.0	6.5±1.1	4.5±0.2	5.2±0.3
BTEX Removal				
Total BTEX				
influent (μg/L)	5398±479	5167±725	2542±370	2411±251
effluent (μg/L)	1.6±0.7	2.1±2.1	2.0±1.0	0.7±0.4
removal (%)	>99.9	>99.9	>99.9	>99.9
Benzene				
influent (μg/L)	1436±140	1452±282	696±95	719±82
effluent (μg/L)	n.d.	n.d.	n.d.	n.d.
Toluene				
influent (μg/L)	2871±224	2400±232	1174±188	1096±105
effluent (μg/L)	n.d.	n.d.	n.d.	n.d.
Xylenes				
influent (μg/L)	1091±234	1326±267	672±94	596±85
effluent (μg/L)	1.4±0.3	1.3±0.8	1.9±0.9	0.75±0.4
Total BTEX removal rate (mg/L bed-day)	1316±133	1321±193	657±98	607±60
DO/BTEX consumption (mg/mg)	3.51±0.41	2.99±0.47	3.5±0.96	3.3±0.69
TCE Removal				
TCE concentration				
influent (μg/L)	373±42	162±27	180±27	58±5
effluent (μg/L)	252±40	111±17	112±6	46±3
removal (%)	32.7±5.1	30.8±7.2	36.3±9.5	19.0±5.8
TCE removal rate (mg/L bed-day)	29.6±4.8	12.9±4.3	17.4±6.7	2.8±1.0
BTEX/TCE consumption (mg/mg)	44.9±4.2	110.9±32.3	41.8±13.8	239±71
Toluene/TCE consumption (mg/mg)	24.0±3.0	52.8±19.4	19.3±6.4	108.7±33.0

3.2.1.1 Test one

On day 83, an experiment was conducted to verify the TCE removal was due to biological activity. The oxygen supply was switched-off. The reactor was fed with the same influent TCE and BTEX concentrations but in the absence of dissolved oxygen for a period of

four hours. Experimental results are presented in Table 3-2. Before the oxygen supply was stopped, the influent and effluent DO concentrations were 22 mg/L and 1.0 mg/L, respectively. Effluent BTEX were below detection limits. TCE removal efficiency averaged 30%. Initially, the influent DO was reduced to 8.9 mg/L by reducing oxygen gas flow. After 10 hours, TCE removal decreased to 10%. The removal of BTEX concurrently decreased from greater than 99.9% to 95%. The effluent BTEX concentration reached 267 μg/L. Subsequently, the oxygen gas supply was completely switched-off and influent DO concentration was reduced to near zero (<0.3 mg/L). After two hours of operation, BTEX removal decreased to 78%; effluent BTEX concentrations increased to 1100 μg/L. No TCE removal was observed at that time. In fact, effluent TCE concentrations were higher than influent TCE concentrations. Afterwards, oxygenated water was restarted and the influent DO concentration was set at 16 mg/L. After two hours of operation, BTEX and TCE removal efficiencies were restored to 96% and 10%, respectively. The influent DO was increased further to 22 mg/L. On the next day (less than 24 hours later), the observed BTEX removal was greater than 99.9% and TCE removal was ca. 28%.

This experiment demonstrated that after more than two month operation, TCE removal of ca. 30% in the reactor was attributable to biological activity and not GAC adsorption. If TCE removal were due to carbon adsorption, TCE removal performance would not have been so dramatically influenced by the cessation of DO in the influent. If TCE removal is performed by aerobic co-metabolic activities, influent DO concentrations will influence TCE removal performance when carbon adsorption is at equilibrium. When DO was absent in the influent, no biodegradation of BTEX and TCE occurred. In this experiment, BTEX removal was still observed but reduced. This removal was due to adsorption onto the GAC. It was interesting that effluent TCE concentration was higher than influent concentration at the same time. This was probably due to the fact that the GAC used has a higher affinity for BTEX than TCE. When BTEX were not degraded, BTEX were sorbed and TCE was displaced from active sorption sites on/in the GAC. As expected, when DO was re-supplied, both BTEX and TCE were again degraded.

Table 3-2. Effect of reducing inlet DO on TCE and BTEX effluent concentrations from the GAC-FBR on day 83.

Activity		8 hrs before reduced DO	10 hrs after reduced DO	2 hrs after O_2 delivery stopped	2 hrs after O_2 restored	12 hrs after O^2 restored
DO	Influent (mg/L)	22.0	8.9	0.3	16.0	23.5
	Effluent (mg/L)	1.0	0.4	0.15	0.4	5.0
TCE	Influent (μg/L)	356	345	360	374	406
	Effluent (μg/L)	249	308	423	336	294
	Removal (%)	30	10	No	10	28
BTEX	Influent (μg/L)	6081	5653	5078	5004	5144
	Effluent (μg/L)	2.2	270	1090	184	0.8
	Removal (%)	>99.9	95	78	96	>99.9

3.2.1.2 Test Two

On day 119, a second experiment was performed to confirm the results obtained on day 83. The samples of influent and effluent were withdrawn for DO, TCE and BTEX determination prior to and after delivery of oxygen was stopped for 2.0, 4.0 and 5.5 hours, respectively. The results of the experiment are summarized in Table 3-3. After delivery of oxygen gas was stopped, influent DO concentration declined from 22.4 mg/L to near zero (<0.3 mg/L). After two hours of operation, BTEX removal was reduced from 99.9% to 61%. Significant amounts of BTEX were detected in the effluent. BTEX removal further decreased to 53% at hours 4 and 5.5. As observed previously, not only was no TCE removal observed in the absence of influent DO, but somewhat higher TCE concentrations were detected in the effluent than influent. This experiment confirmed that the TCE removal in the GAC-FBR was due to aerobic biological activities. The higher TCE concentrations in effluent than influent are due to the competitive adsorption of BTEX and TCE for GAC.

Table 3-3. Effect of reducing inlet DO on TCE and BTEX effluent concentrations from the GAC-FBR on day 119.

Activity		Before O_2 delivery stopped	2 hrs after O_2 delivery stopped	4 hrs after O_2 delivery	5.5 hrs after O_2 delivery stopped
DO	Influent (mg/L)	22.4	0.3	0.4	0.4
	Effluent (mg/L)	3.8	0.2	0.2	0.2
TCE	Influent (μg/L)	188	188	174	176
	Effluent (μg/L)	125	255	245	230
	Removal (%)	34	No	No	No
BTEX	Influent (μg/L)	5128	5399	5106	5177
	Effluent (μg/L)	0.3	2100	2400	2435
	Removal (%)	>99.9	61	53	53

3.2.2 Operational Results - Test Period I

From day 10 to day 95, the reactor received influent TCE of ca. 380 μg/L and BTEX of ca. 6000 μg/L. Throughout this period, high BTEX removal efficiency (> 99.9%) was observed. No benzene or toluene was detected in reactor effluent (Figures 3-4 and 3-5); only a trace amount of xylene (<2 μg/L) was detected (Figure 3-6). TCE removal efficiency, initially was high (>60%). This gradually decreased and eventually stabilized at approximately 30% (Figure 3-8). The initial high TCE removal efficiency was caused by the adsorption onto the GAC. As adsorption onto the GAC reached equilibrium for TCE, effluent TCE concentrations and reactor TCE removal stabilized. TCE removal in the reactor after this was dependent on biological degradation via co-metabolism of TCE.

The results of steady-state conditions for Period I (operational data from days 85 to 92) are summarized in Table 3-1. All important operational parameters including temperature, HRT, pH, influent and effluent concentrations of DO, BTEX, and TCE are presented here. During steady-state I, the average TCE removal was 32.7%; more than 99.9% removal of BTEX was concurrently observed. The volumetric BTEX and TCE removal rates were 4.1 Kg COD/m^3-d and 29.6 mg/L-d, respectively. The BTEX/TCE and toluene/TCE consumption ratios were ca. 45 and 24 mg/mg, respectively.

Typical profiles of DO, BTEX and TCE for this steady-state condition (day 90) showed most removal of BTEX occurred at the bottom (0-1.5 m bed height) of the fluidized bed (Figure 3-9). Above 1.5 m where BTEX concentrations were essentially nil, oxygen consumption continued. The oxygen consumption in the upper portion of the fluidized bed could possibly be related to degradation of BTEX sorbed by the GAC, degradation of TCE and endogenous respiration of the biofilm. TCE removal was observed throughout the fluidized bed. TCE removal was higher in the upper portion of the bed (in the absence of BTEX).

3.2.3 Operational Results - Test Period II

From day 96 to day 137, the reactor influent TCE concentration was set at ca. 160 μg/L and BTEX at ca. 6000 μg/L. This resulted in the BTEX/TCE loading ratio being increased by 100% compared with previous test period. If TCE removals were limited by lack of energy source from BTEX degradation during the previous test (day 10 to day 96), the increase in BTEX/TCE ratio or decrease in TCE loading rate would result in an improvement in TCE removal efficiency. If TCE removal was not limited by availability of substrates (BTEX), no improvement in TCE removal efficiency should be observed.

The operational results of TCE concentrations in influent and effluent and TCE removal efficiency are presented in Figure 3-10. During the first week, TCE removal efficiency appeared poor due to the release of TCE sorbed on the GAC during the period of higher inlet TCE concentrations. After 10 days of operation, TCE removal stabilized at approximately 30%. The results of steady-state conditions with an influent of ca. 160 μg TCE/L are summarized in Table 3-1, using operational data from days 117 to 137. Under these operational conditions, the average TCE removal was 30.8% with a volumetric removal rate of 12.9 mg/L-day. More than 99.9% of influent BTEX were removed at a volumetric rate of 4.1 Kg COD/m^3-d. The BTEX/TCE and toluene/TCE consumption ratios were ca. 111 and 53 mg/mg, respectively. The experimental results indicated that reduction in the influent TCE concentration and, therefore, increase in the BTEX/TCE loading ratio, did not improve TCE removal efficiency. This suggests that TCE removal efficiency in the reactor was not limited

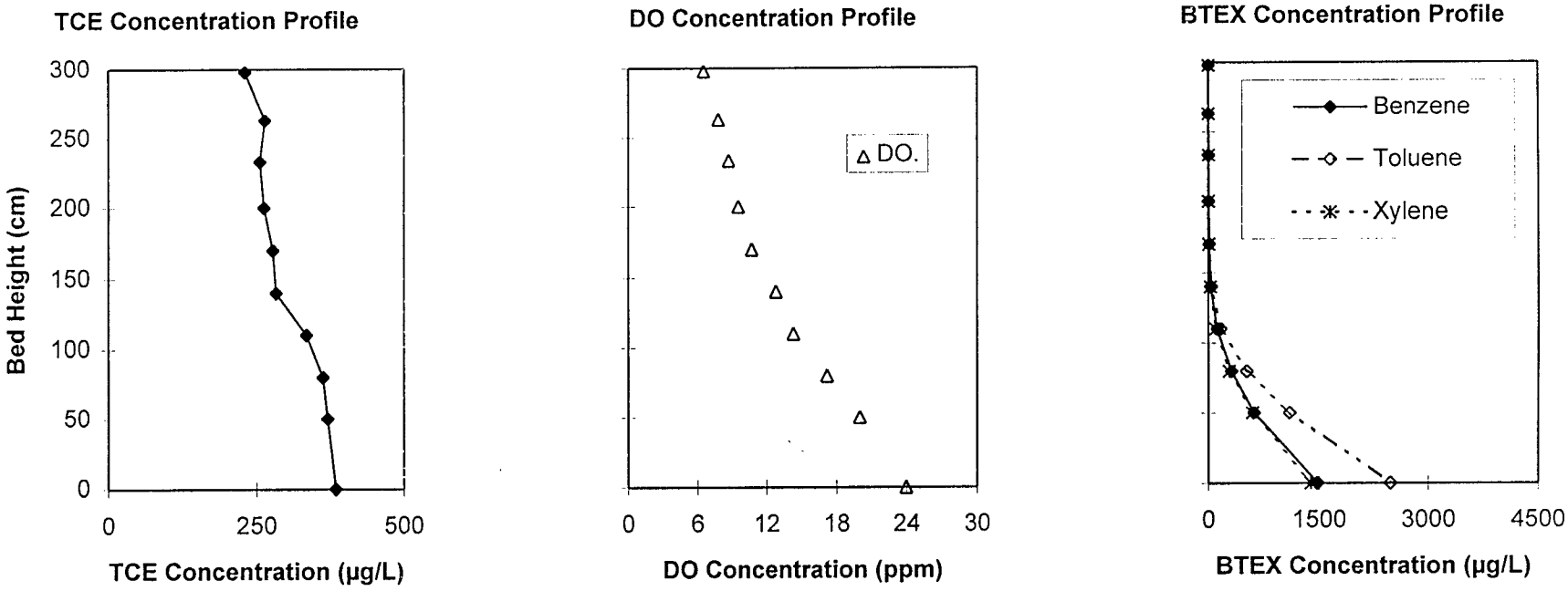

Figure 3-9. Profiles of TCE, DO and BTEX through the GAC-FBR system (day 90).

by the amount of BTEX supplied or co-metabolic capacity of the biofilm. This hypothesis is supported by batch TCE degradation assays reported in Section 4.

Typical profiles of DO, BTEX and TCE for this steady-state condition (day 136) are presented in Figure 3-11. As observed previously, most removal of BTEX occurred within the bottom 1.5 m of fluidized bed. DO consumption and TCE removal were observed throughout the entire bed, with greater removal occurring in the zone with low BTEX concentrations.

3.2.4 Operational Results - Test Period III

From days 138 to 158, the reactor influent TCE concentration was set at ca. 180 μg/L and BTEX at ca. 3000 μg/L. The ratio of BTEX/TCE supplied was reduced by 50% compared with previous test period (day 96-137) in order to examine whether TCE removal efficiency was influenced by reducing BTEX. As reported in the literature (Folsom and Chapman, 1991; Landa et al., 1994), toluene and TCE are competitive substrates (i.e. TCE degradation is reduced in the presence of toluene). When TCE degradation is not limited by supply of substrates to the biofilm, TCE removal efficiency in the reactor would presumably be increased if less BTEX were supplied (less substrate competition).

The operational results from this period are presented in Figure 3-12. The results of steady-state conditions are summarized in Table 3-1, using operational data obtained from days 146 to 154. Under this operational condition, the average TCE removal was 36.3% at a volumetric TCE removal rate of 17.4 mg/L-d. More than 99.9% of influent BTEX were removed at a volumetric BTEX removal rate of 2.1 Kg COD/m^3-d. The BTEX/TCE and toluene/TCE consumption ratios were ca. 42 and 19 mg/mg, respectively. The experimental results indicated that the decrease in BTEX/TCE loading ratio did result in a slight improvement in TCE removal performance as expected.

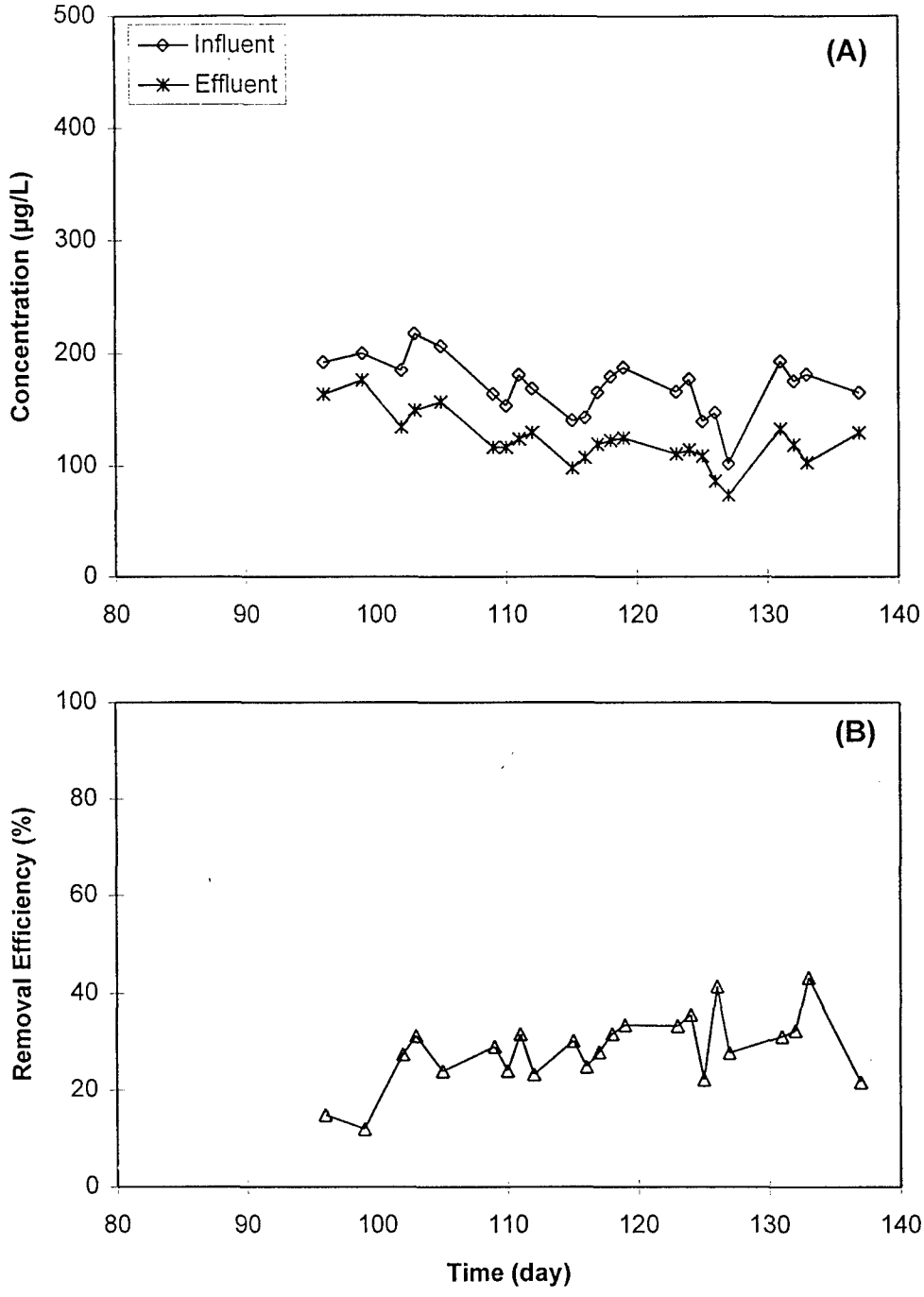

Figure 3-10. TCE concentrations in reactor influent and effluent (A) and TCE removal efficiency (B) during operational period II (days 96 to 137).

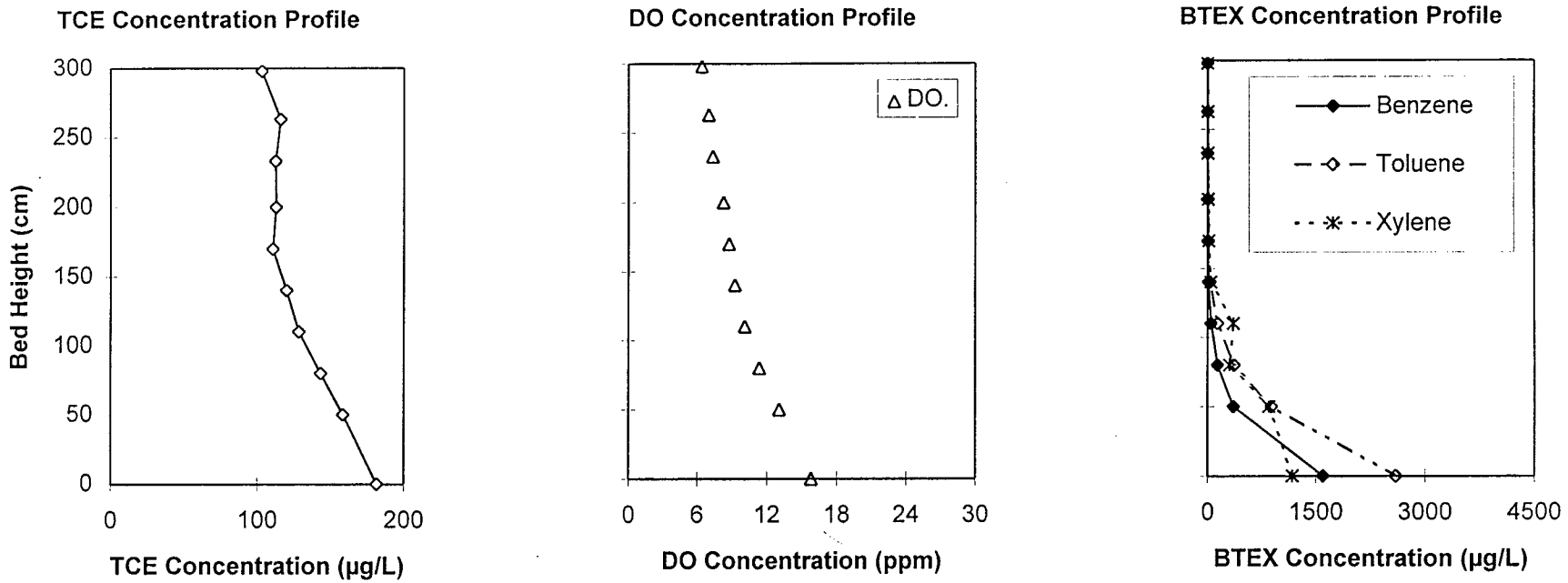

Figure 3-11. Profiles of TCE, DO and BTEX through the GAC-FBR system (day 136).

The profiles of DO, BTEX and TCE for this steady-state condition (day 155) are presented in Figure 3-13. The reduction in influent BTEX concentrations by 50% did not significantly reduce the BTEX penetration level in the fluidized bed. The BTEX was observed almost up to the 1.5 m bed height although at slightly lower concentrations than observed previously (Figures 3-9 and 3-11). DO consumption was observed throughout the bed. TCE removal, however, did not occur to any measurable extent above the 2.5 meter height.

3.2.5 Operational Results - Test Period IV

From days 159 to 182, the reactor influent TCE concentration was set at ca. 60 μg/L and BTEX at ca. 3000 μg/L to investigate TCE removal with a relatively low influent TCE concentration. The influent BTEX concentration was maintained at the same level as previously. The BTEX/TCE loading ratio, therefore, was increased by three times compared with the previous test period (days 138-158). The average HRT was 5.7 minutes.

The operational results of TCE concentrations in influent and effluent and TCE removal efficiency are presented in Figure 3-14. The steady-state results are summarized in Table 3-1, using operational data obtained from days 168 through 177. The temperature in the reactor was 18°C. Under these operational conditions, the average TCE removal efficiency was 19% at a volumetric TCE removal rate of 2.8 mg/L-d. The BTEX volumetric loading rate was 1.87 Kg COD/m^3-d; BTEX removal efficiency was greater than 99.9% The BTEX/TCE and toluene/TCE consumption ratios were ca. 239 and 109 mg/mg, respectively. The experimental results indicated that the GAC-FBR can remove TCE even at low influent TCE concentrations (ca. 60 μg/L). TCE removal efficiency during this period, however, was lower than those observed previously. The relatively low TCE removal could be caused by low temperatures (18°C) during the test period and relatively high BTEX/TCE ratio (173 mg/mg) in reactor influent.

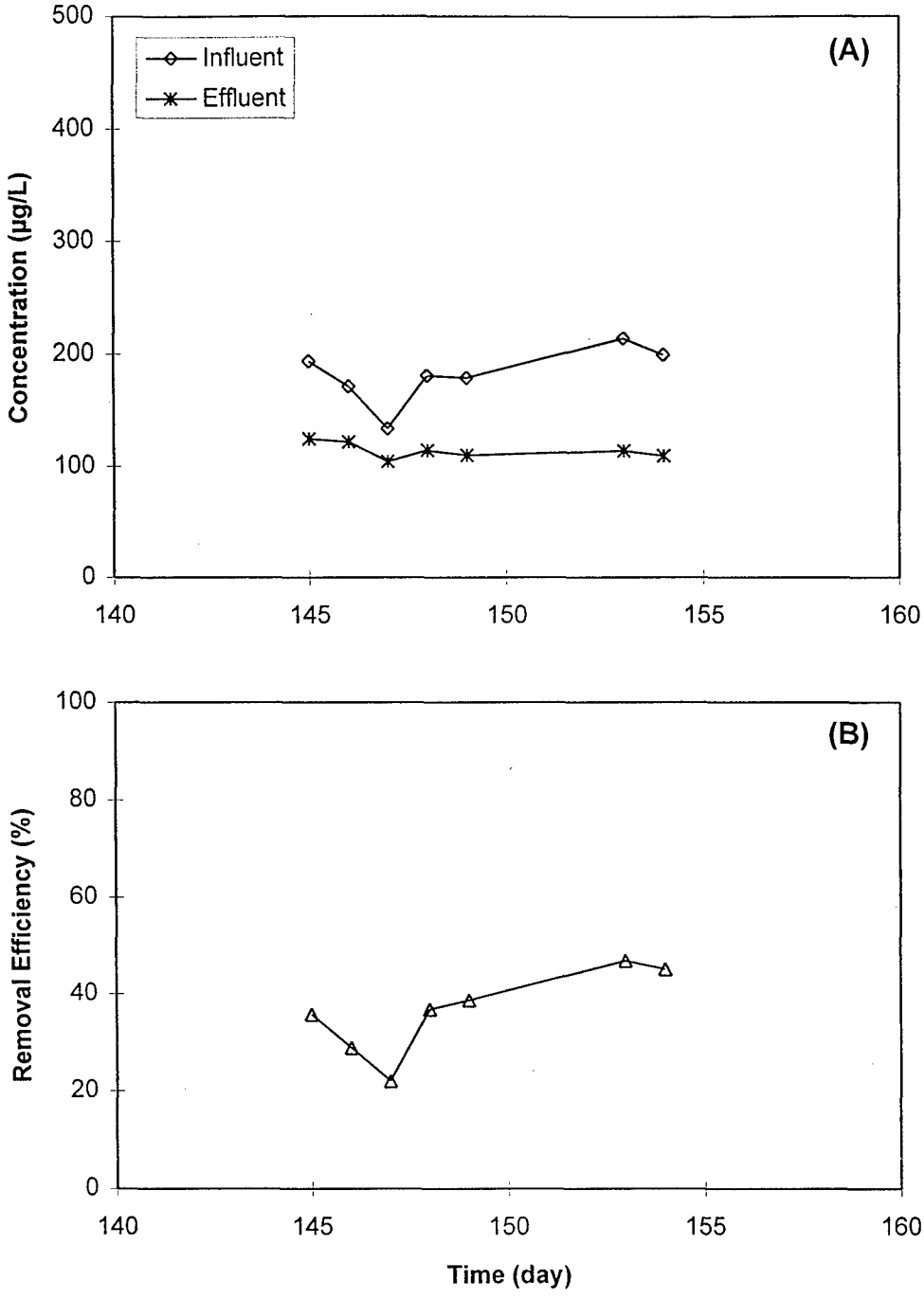

Figure 3-12. TCE concentrations in reactor influent and effluent (A) and TCE removal efficiency (B) during operational period III (days 146 to 154).

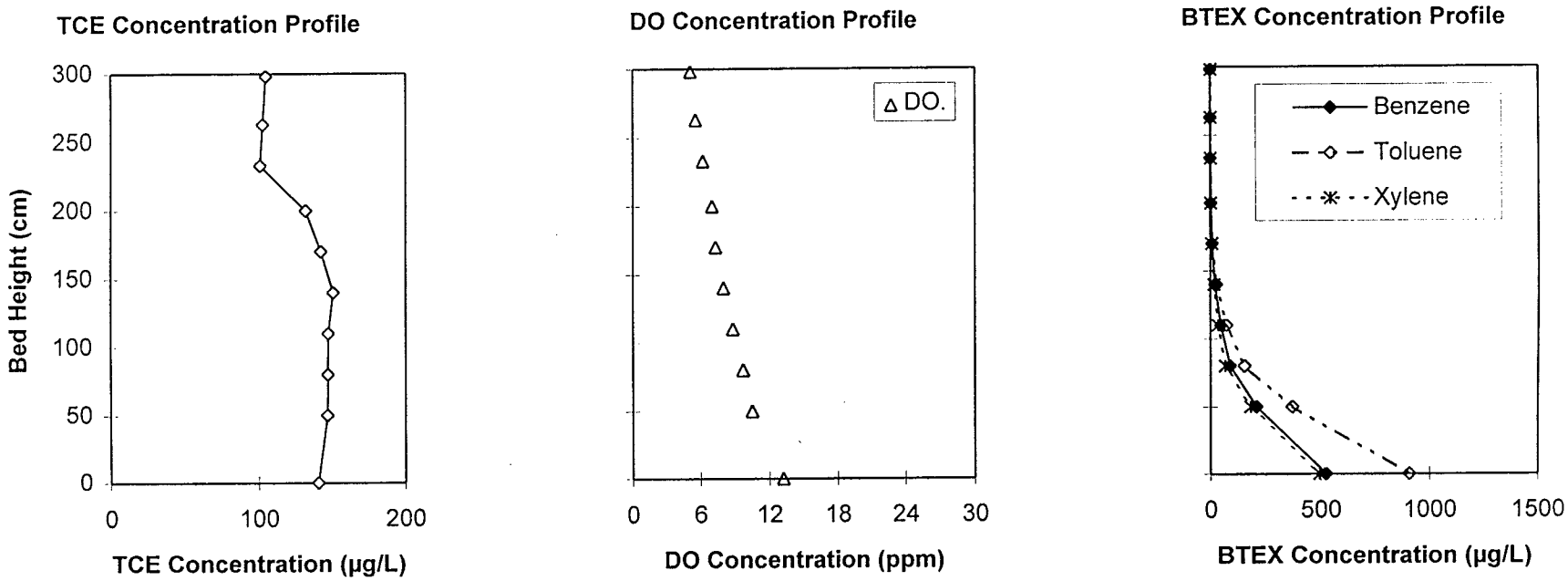

Figure 3-13. Profiles of TCE, DO and BTEX through the GAC-FBR system (day 155).

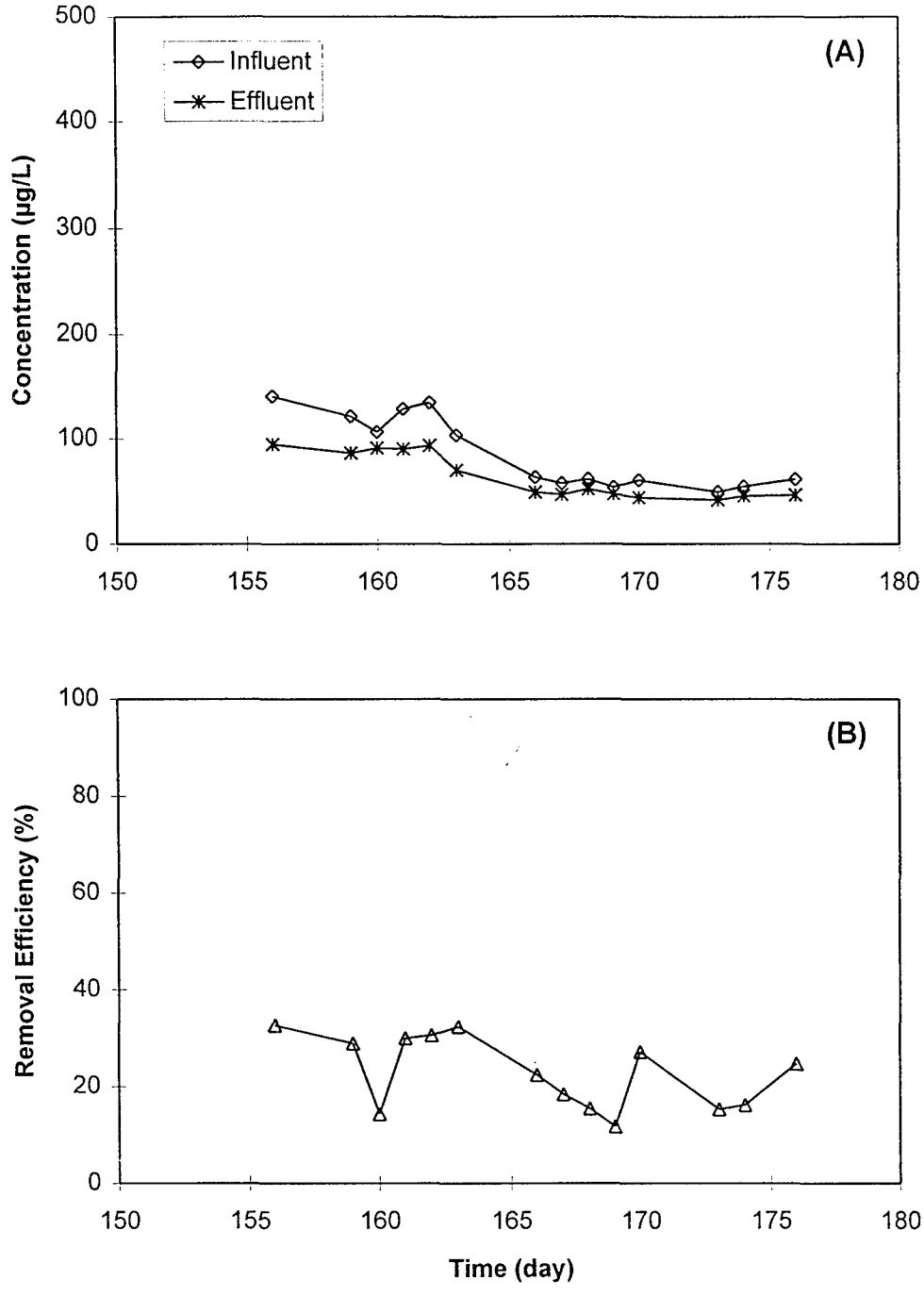

Figure 3-14. TCE concentrations in reactor influent and effluent (A) and TCE removal efficiency (B) during operational period IV (days 159 to 177).

4. CHARACTERIZATION OF KINETIC CAPACITY OF BIOFILM BIOMASS

4.1 Co-metabolic TCE Degradation

4.1.1 Influence of BTEX on TCE degradation rate

Headspace-free, batch assays, with biomass taken from the GAC-FBR, indicated that co-metabolic TCE degradation occurred at a reduced rate in the presence of BTEX (>1600 μg/L), compared to assays conducted with no added BTEX. No TCE degradation was observed in the abiotic (no biomass added) control reactors. The results of a typical time course assay for TCE degradation in the presence and absence of added BTEX are presented in Figure 4-1 and Table 4-1. With added BTEX, TCE degradation was slow during the initial 30 minutes. The rate increased when the added BTEX was consumed. No lag in TCE degradation was observed without added BTEX. This indicated that co-metabolic TCE degradation by the biomass from the reactor was inhibited by the presence of BTEX. This observation is consistent with the test results using pure cultures (Landa et al., 1994).

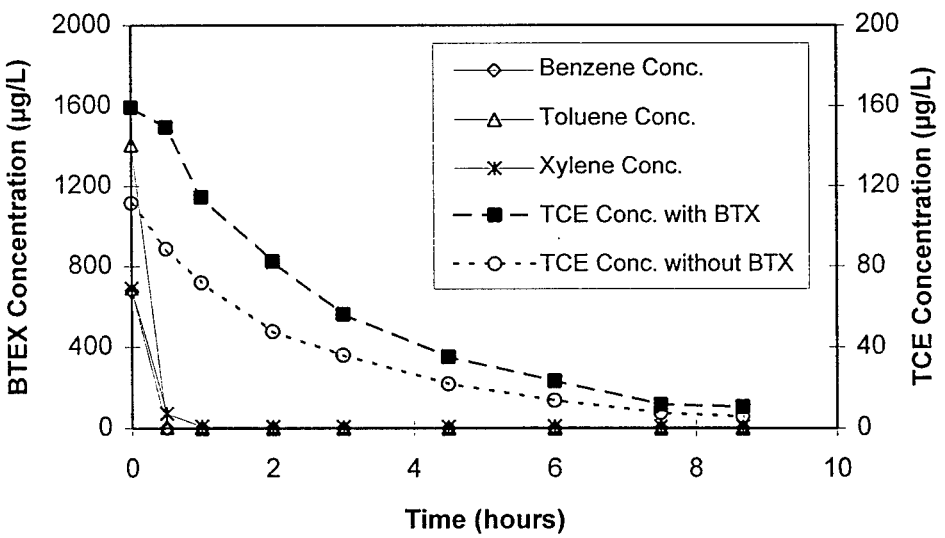

Figure 4-1. Results of bench assays conducted in headspace free syringe reactors using biomass from the GAC-FBR system on 10/3/95.

Table 4-1. The changes in TCE and BTEX concentrations during a batch assay using biomass from the GAC-FBR system.

	Reactor No. 1				Reactor No. 2
Time	Benzene (μg/L)	Toluene (μg/L)	Xylene (μg/L)	TCE (μg/L)	TCE (μg/L)
0	677	1408	690	159	112
0.5	0.2	5.8	73	149	87
1.0	BDL	2.2	9.0	115	72
2.0	BDL	BDL	BDL	82	48
3.0	BDL	BDL	BDL	56	36
4.5	BDL	BDL	BDL	35	22
6.0	BDL	BDL	BDL	23	14
7.5	BDL	BDL	BDL	11	7.6
8.7	BDL	BDL	BDL	10	5.8

Note:
(1) This test was performed at 22°C with 0.0104 gVSS/L biomass concentrations in 100-ml, non-headspace batch reactors. Initial pH was 7.0. Biomass was obtained from the GAC-FBR on operational day.
(2) Reactor No.1 with added BTEX while reactor No.2 without added BTEX.
BDL - below detection limit (<1 μg/L).

4.1.2 TCE degradation kinetics

In this study, co-metabolic TCE degradation kinetics at concentrations (<1000 μg/L), frequently observed in contaminated groundwater, were examined. Based on the results obtained from batch assays in the absence of added BTEX, TCE degradation could be described by a first order reaction, expressed as

$$dS / dt = -kSX \qquad \textbf{(4-1)}$$

or

$$S / S_o = \exp(-kXt) \qquad \textbf{(4-2)}$$

where, S = TCE concentration (mg/L) at time t, S_0 = initial TCE concentration, t = time (hr), k = a constant, and X= biomass concentration (gVSS/L). The change in biomass concentration during the batch assay was negligible and was ignored. A constant value of k can be calculated by plotting the $\ln(S/S_0)$ versus Xt, using time course data from each batch assay. Illustrated in Figure 4-2 is the regression data of two assays using the biomass obtained from the GAC-FBR on day 125 and day 131. Values of the k are presented in Table 4-3. The value of k was observed to be influenced by the BTEX/TCE or toluene/TCE consumption ratio. With a higher

BTEX/TCE consumption ratio (110 mg BTEX/mg TCE or 55 mg toluene/mg TCE), the k values (2.77-3.52 l/gVSS-hr) was almost five times greater than those obtained (0.59 l/gVSS-hr) with the lower BTEX/TCE consumption ratio (42 mg BTEX/mg TCE or 20 mg toluene/TCE).

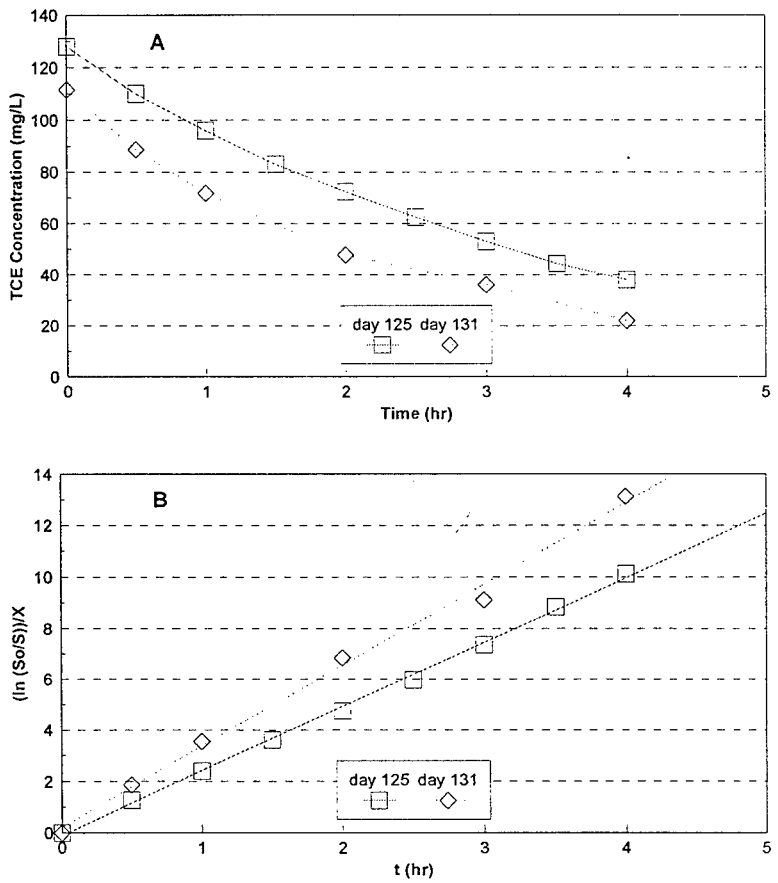

Figure 4-2. Regression data of two assays using the biomass obtained from the GAC-FBR on days 125 and 131.

Table 4-2. Initial TCE degradation rate in the presence or absence of BTEX.

Batch Assay Reactor	Data Used	Conditions	TCE degradation Rate (mg TCE/gVSS-hr)
No.1	From time zero to 0.5 hr	Presence of BTEX	1.90
	From 0.5 hr to 2.0 hr	BTEX consumed	4.30
No.2	From time zero to 1.0hr	No BTEX added	3.82
Note: the data used is from Table 4-1.			

Table 4-3. Comparison of k values for TCE degradation by biomass obtained from the GAC-FBR fed at different BTEX/TCE loading ratios.

Steady-state Period	BTEX/TCE Loading Ratio (mg/mg)	BTEX/TCE Consumption Ratio (mg/mg)	k Value (l/gVSS-hr)
II	37	111	2.77
II	37	111	3.52
III	17	42	0.59

The results of a TCE degradation test with three different initial concentrations is presented in Figure 4-3A. The biomass used was obtained on day 146 (Period III) when the reactor received an influent BTEX/TCE loading ratio of 17 mg/mg and BTEX/TCE consumption ratio of 42 mg/mg was achieved. The initial TCE degradation rates at the three concentrations shows a linear relationship between rate and TCE concentration. By plotting the average TCE degradation rate during initial two hours, a k value of 0.59 l/gVSS-hr was obtained (regression coefficient 0.999).

The batch assay results indicated that co-metabolic TCE degradation activity of the biofilm biomass was dependent on the concentration of BTEX and TCE used or the BTEX/TCE consumption ratio. Lower BTEX/TCE consumption rates indicate that, on a percentage-basis, more enzymes were inactivated by TCE during TCE degradation, resulting in lower TCE degradation activity of the biomass. However, the TCE degradation activity still remained at a significant level when BTEX/TCE consumption ratio and toluene/TCE consumption ratio were 42 and 21 mg/mg, respectively. This suggests that the biomass in the reactor was still highly active. In addition, the average activity of biomass in the reactor is probably higher than reported herein. The biomass used for these assays was obtained from the upper portion of the fluidized bed, and had likely lost more enzymatic activity and reducing power than the biomass in the lower portion of the bed. Values of kinetic constants obtained can, therefore, be considered conservative, but representative of what occurred in the reactor. Most transformation of TCE occurred in the upper portions of the fluidized bed where the primary substrates were depleted. Substrate competition by toluene and phenol degraders has been reported (Folsom et al., 1990).

4.2 *Biodegradation of Chlorinated Ethylenes*

The capability of co-metabolic degradation of chlorinated ethylenes including TCE, 1,1-DCE, *cis*-1,2-DCE, *trans*-1,2-DCE and VC was tested in 65-ml test vials at ambient temperatures (20-22°C). The same amount of chlorinated ethylenes were added into replicate vials. A comparison of initial degradation rates for different chlorinated ethylenes is presented in Figure 4-4 and Table 4-4. The biomass used was collected from the GAC-FBR at day 173 (Period IV). At that time, the reactor was fed with an influent concentration of ca. 60 μg TCE/L and 3000 μg BTEX/L. The BTEX/TCE loading ratio at the time was 50 mg/mg. The biomass from the GAC-FBR was capable of degrading all chlorinated ethylenes tested. The sequence (highest first) of initial degradation rate was *cis*-1,2-DCE > VC > TCE > *trans*-1,2-DCE >1,1-DCE (Figure 4-4). The co-metabolic degradation capacity for different chlorinated ethylenes was dependent upon the operational TCE/BTEX loading ratio and BTEX/TCE consumption ratio. However, the sequence of the capacity (highest to lowest) was VC > *cis*-1,2-DCE > TCE > *trans*-1,2-DCE > TCE (Table 4-4). This indicated that transforming the lesser chlorinated ethylenes was less inhibitory to the microorganisms. The exception to this was 1,1 DCE which was not transformed to any significant extent (Figure 4-4).

Cis-1,2-DCE and VC are major anaerobic dechlorination intermediates of PCE and TCE and are frequently observed at many contaminated sites (Freedman et al., 1989; De Briun et al., 1992; DiStefano et al., 1992; Wu et al., 1993). The results of this study demonstrated that the GAC-FBR can be utilized to treat groundwater contaminated with not only TCE but also other less-chlorinated ethylenes. Higher rates and removal efficiencies will be expected if *cis*-1,2-DCE and VC are treated using GAC-FBR co-metabolic process compared to TCE.

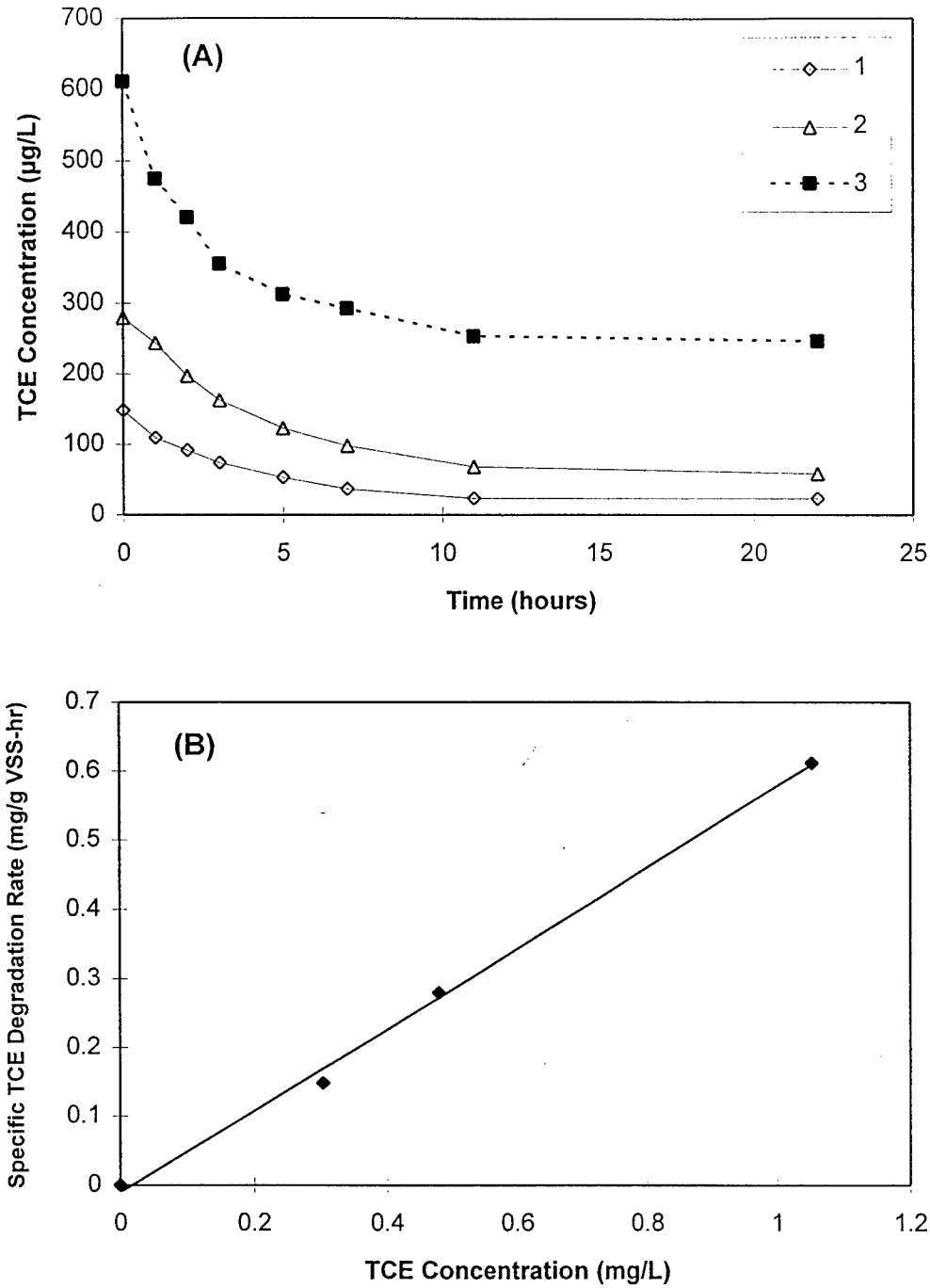

Figure 4-3. Time course of TCE degradation (A) at three different initial TCE concentrations and (B) specific degradation rates based on the results of assays shown above.

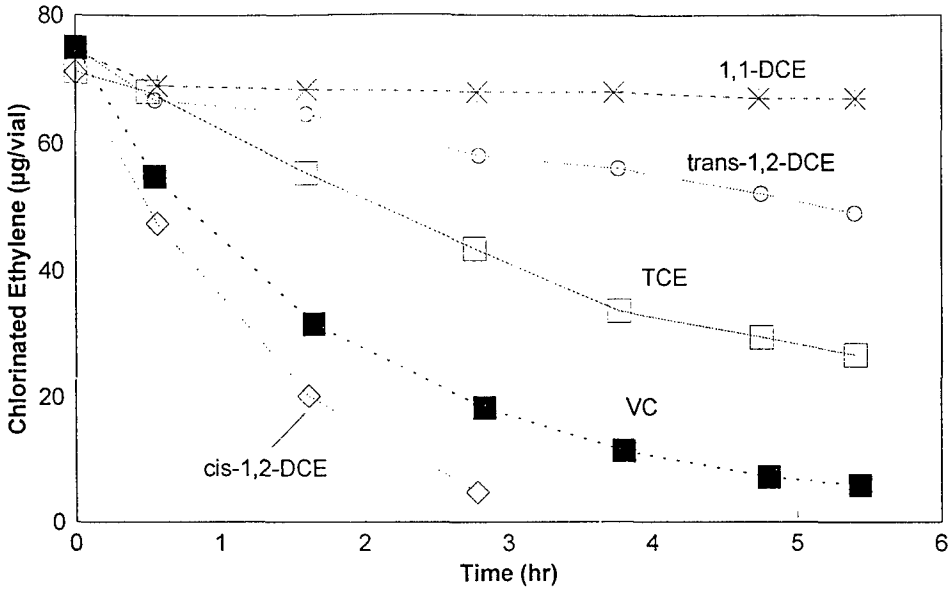

Figure 4-4. Transformation of different chlorinated ethylenes by biomass taken from the GAC-FBR reactor.

Table 4-4. TCE degradation rates and degradation capacity for different chlorinated ethylenes.[1,2]

Compounds	TCE	*cis*-1,2-DCE	*trans*-1,2-DCE	Vinyl Chloride
Initial degradation rate (mg/gVSS-hr)	0.59	1.87	0.36	1.19
Degradation capacity[3] (mg chlorinated ethylene/gVSS)	9.3	14.8	6.6	17.2

[1]The results were obtained using batch assay in 65 ml vials with 30 ml of disrupted biofilm (0.563 gVSS/L). The test conditions were: temperature 22°C, pH 7.0, with 75µg respective chlorinated ethylene per vials.
[2]The time courses of the assay are illustrated in Figure 4-3A-D.
[3]The degradation capacity was estimated after 68 hr incubation by using the following equation: capacity = amount of chlorinated ethylene removed (mg)/biomass inoculated (gVSS).

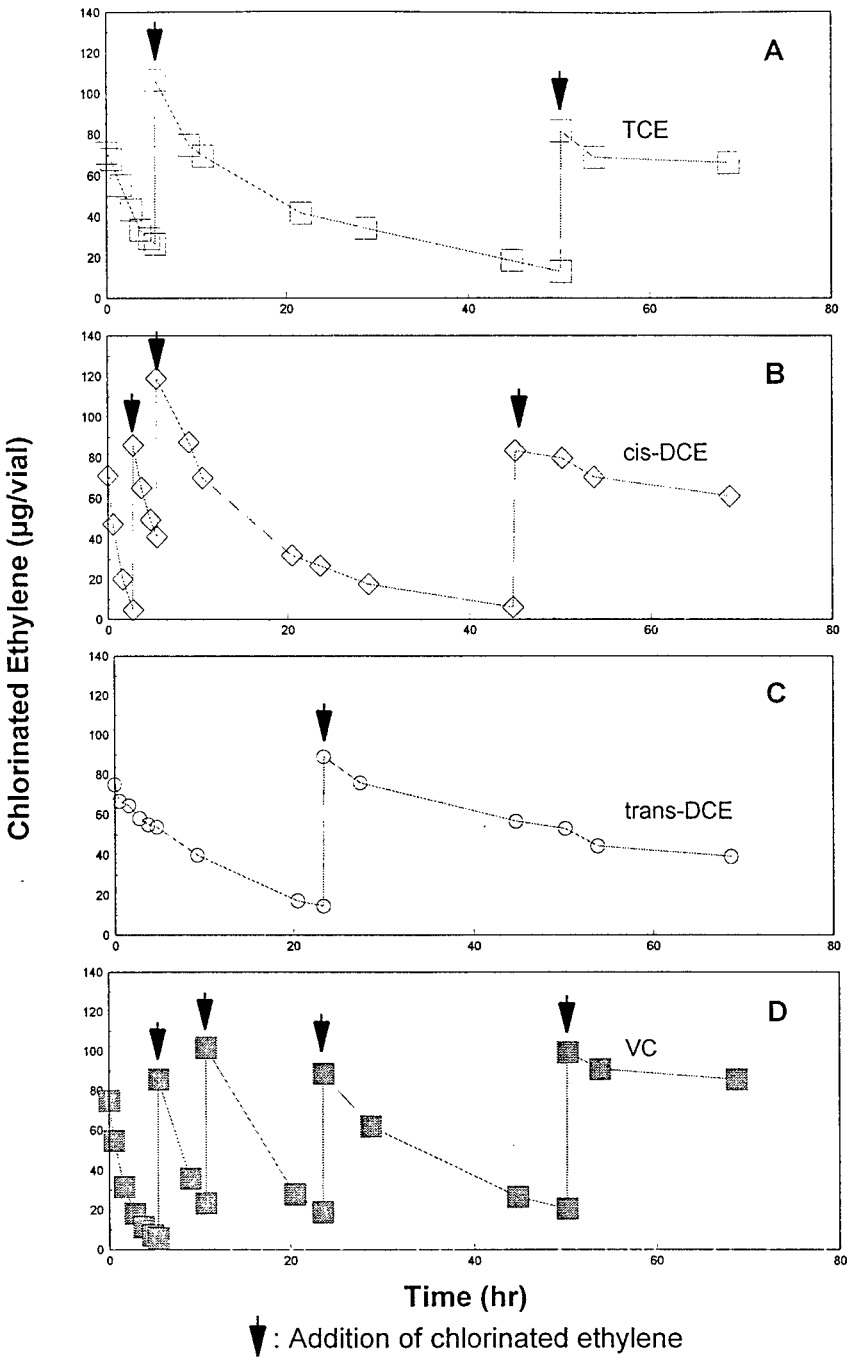

Figure 4-5. Results of assays performed to estimate the transformation capacity of biomass from the GAC-FBR for different chlorinated ethylenes.

5. MODELING AND PERFORMANCE ESTIMATION

The results obtained from reactor operation and batch assays provided valuable information to estimate TCE removal capabilities of the GAC-FBR. In this section of the report, the information collected was used to develop a simple model to estimate process performance.

5.1 Estimation of Reactor Performance

TCE removal performance at different influent concentrations can be estimated using the data obtained from the four steady-state conditions described in Section 3.

Based on the results obtained, the influent BTEX/TCE ratio had only a slight effect on TCE removal efficiency. The mean volumetric TCE removal rate, (as mg TCE/liter of fluidized bed per day) in Table 3-1, appeared most dependent on the influent TCE concentration. A plot of the mean volumetric TCE removal rates versus average influent TCE concentration is presented in Figure 5-1. Results show a linear relationship between these two parameters. This suggests that the removal of TCE in the fluidized bed, in the limited range of conditions tested, can be adequately described using a first order reaction expression. This is supported by the results obtained using batch assays in Section 4.1. The empirical relationship can be expressed as:

$$r = k \bullet S_{in} \qquad (5\text{-}1)$$

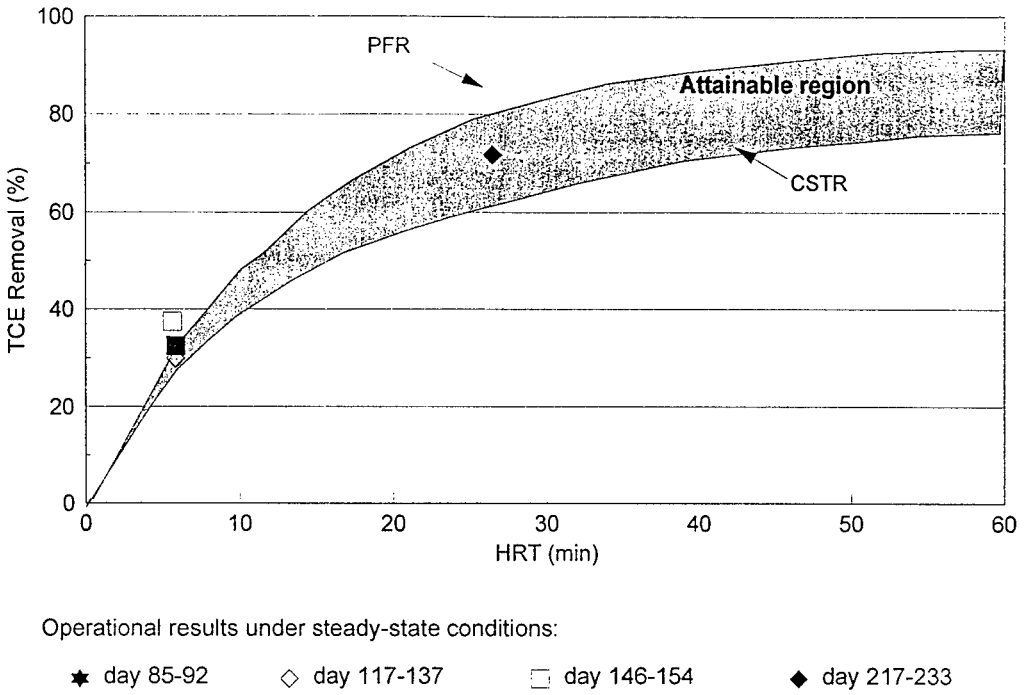

Figure 5-1. TCE removal efficiency versus average influent TCE concentration.

where, r = average volumetric TCE removal rate (mg/L-day), k = constant (1/day), and S_{in} = influent TCE concentration (mg/L). Based on the data obtained for the laboratory-pilot unit, a k value of 82.5/day with a regression coefficient of 0.99 was obtained. This relationship can be utilized to estimate the reactor performance with different influent TCE concentrations under similar environmental and nutrition conditions i.e.:

- Temperature 18-24°C, pH 6-7 in reactor, HRT 5.6-5.7 min, and
- BTEX/TCE consumption ratio of 20-50 mg/mg, similar C:N:P in influent.

Because the volumetric TCE removal rate can be written as

$$r=(S_{in}-S_{eff})Q/V=(S_{in}-S_{eff})/\Theta \qquad \textbf{(5-2)}$$

where, S_{eff} is effluent TCE concentration (mg/L), Q is the flow rate (l/day), V is the volume of the fluidized bed region (liter), and Θ is hydraulic retention time of the fluidized bed region (days). Therefore, the relation can be obtained from equations (5-1) and (5-2):

$$(S_{in} - S_{eff}) / \Theta = kS_{in} \qquad \textbf{(5-3)}$$

$$S_{eff} = S_{in}(1 - k\Theta) \qquad \textbf{(5-4)}$$

and

$$\eta = k\Theta \qquad \textbf{(5-5)}$$

where, η is TCE removal efficiency (x100%), k = 82.5/day and Θ=0.00388 day (or 5.6 min). Based on the results obtained in this study, the TCE removal efficiency is:

$$\eta = k\Theta = 32\%$$

This estimated value is close to experimental results obtained using influent TCE concentrations from 160 to 380 μg/L. The above empirical equations may be modified using HRT as a variable.

5.2 *Estimation of Reactor Performance Based on Batch Assay Data*

The GAC-FBR system is a continuous feed reactor. Its flow pattern is between two typical reactor types i.e. continuous stirring reactor (CSTR) and plug flow reactor (PFR) but much more complicated than these two types. In order to simplify the estimation calculation, we assumed that reactor TCE removal performance is between CSTR and PFR systems. The TCE removal performance for the GAC-FBR could vary within a range between CSTR and PFR systems.

The parameters used for the simulation are:

- BTEX/TCE consumption ratio is 42 mg/mg or toluene/TCE ratio is 21 mg/mg;

- TCE degradation follows the first order reaction with k value of 0.59 l/gVSS-hr in the entire fluidized bed;
- The influence of diffusivity from bulk liquid into cells is ignored;
- Average biomass concentration in the fluidized bed is 5 gVSS/L;
- A coefficient (α) of 1.42 is used to conservatively estimate average biomass activity. We assumed that the biomass from the upper portion of fluidized bed had 70% of average activity.

For CSTR system, the relationship of influent and effluent TCE concentration can be expressed as:

$$S_{eff} / S_{inf} = 1 / (1 + \alpha k \Theta X) \qquad \textbf{(5-6)}$$

where, S_{eff} and S_{inf} are TCE concentrations (mg/L) in the effluent and influent, respectively; α is coefficient for biomass activity; k = 0.59 l/gVSS-hr, reaction constant; Θ is HRT for fluidized bed (hr); and X = 5 gVSS/L, average biomass concentration in fluidized bed.

For PFR system, the relationship of influent and effluent TCE concentration can be expressed as:

$$S_{eff} / S_{inf} = \exp(-\alpha k \Theta X) \qquad \textbf{(5-7)}$$

Using the above values, the calculated TCE removal efficiencies versus different HRT for the two typical reactor systems are presented in Figure 5-1, and Table 5-1. Higher TCE removal efficiency can be obtained in the PFR system than the CSTR system for the same HRT. TCE removal efficiency by the GAC-FBR can be assumed to fall within the "attainable" region between performance curves of CSTR and PFR systems (Figure 5-1). With an HRT of 5.6 minutes, estimated TCE removal was 28 and 32% for CSTR and PFR systems, respectively. These estimated values are close to the TCE removal values obtained in the laboratory-pilot GAC-FBR (Table 3-1). If a longer HRT were to be used, the TCE removal in the GAC-FBR

would be increased. For example, if the HRT were 30 minutes, TCE removal is predicted to be between 67.8 and 87.8%. A TCE removal efficiency of between 76.0 and 95.8% could be obtained with 45 minute HRT.

Table 5-1. Estimated TCE removal performance in a GAC-FBR based on batch assay results.

	TCE Removal (%)	
Hydraulic Retention Time of Fluidized Bed (minutes)	**CSTR System**	**Plug Flow System**
5.6	28.1	32.3
10.0	41.3	50.5
15.0	51.3	65.1
20.0	58.4	75.5
30.0	67.8	87.8
40.0	73.7	94.0
50.0	77.8	97.0
60.0	80.8	98.5

In general, FBRs behave much closer to PFR than CSTRs. Results obtained will, therefore, be closer to that at the higher portion of "attainable" regions in Figure 5-1.

5.3 Comparison of TCE Removal using BTEX Compared with other Primary Substrates

Aerobic co-metabolic TCE removal can be performed by different aerobic microorganisms including methane-oxidizing, phenol/toluene-oxidizing, ammonia-oxidizing, and alkene-oxidizing organisms. Currently, methane, phenol, and toluene can be used as primary substrates for the growth of bacteria with different oxygenases able to transform TCE. Based on published data, typical substrate requirements are 60 mg methane/mg TCE (Avarez-Cohen and McCarty, 1991a, 1991b), 20-30 mg toluene/mg TCE (Landa et al., 1994), and 16-30 mg phenol/mg TCE (Hopkins et al., 1993; Segar et al., 1995). The costs of adding these substrates to soils or contaminated aquifers needs to be considered. The addition of toluene and phenol may have environmental regulation problems since both are hazardous chemicals. TCE and toluene (and other petroleum hydrocarbons) are, however, found as co-contaminants at many sites. In these situations, utilization of toluene as a substrate for TCE removal can be

considered a benefit; no costs for the substrate is required and two contaminants are being removed concurrently.

Based on the data from the GAC-FBR, significant TCE removal was achieved at BTEX/TCE and toluene/TCE consumption rates as low as 42 and 21 mg/mg, respectively. The biomass taken from the reactor still had significant co-metabolic TCE degradation activity (see Section 4). Based on research using a pure culture of toluene-oxidizing *Pseudomonas cepacia* G4, a toluene/TCE consumption ratio as low as 14 mg/mg was possible (Landa et al., 1994). The TCE degradation capacity of the mixed culture biomass in this study was close to that of this pure culture. Our study also indicates that the GAC-FBR can maintain a stable TCE-degrading microbial population; TCE removal performance was maintained for more than six months of operation.

The role of benzene and xylene in TCE transformation is not clear. Pure culture studies indicated that a *Pseudomonas* strain grown on benzene oxidized toluene rapidly but toluene-grown cells oxidized benzene very slowly, suggesting that the benzene dioxygenase is distinct from the dioxygenase induced by toluene (Haigler et al. 1992). To date, we do not know whether benzene and xylenes can be utilized by microorganisms in the biofilm to synthesize oxygenases which are capable of degrading TCE and other chlorinated hydrocarbons. Kampbell and Wilson (1994) reported that TCE and VC were degraded in soil microcosms by adding the volatile components of gasoline as the primary substrates.

6. REACTOR PERFORMANCE TEST WITH EFFLUENT RECYCLE

From day 183 to day 233, the reactor was operated with recirculation to examine TCE removal performance at a longer HRT and test the modeling estimation results from Section 5.2. During this period, the reactor influent contained the same ratio (benzene:toluene:xylenes = 1:2:1) as that used previously.

Steady-state results are summarized in Table 6.1, using operational data from days 217 to 233. The average influent TCE concentration was ca. 48.3 μg/L and influent BTEX concentration was ca. 8330 μg/L. The reactor was operated at an average overflow rate of 261 ml/min and, therefore, with a longer HRT (27 min) than previously used. During this operational period, it was impossible to directly determine the influent pH and concentrations of DO, BTEX and TCE because the BTEX-TCE solution, oxygenated water, nutrient solution and recycled reactor effluent were mixed together in the feed mixing reservoir. The DO concentrations and pH in the feed mixing reservoir and effluent are presented in Table 6.1. To preclude volatilization of TCE and BTEX, oxygenation of the recycled stream was not performed. Accordingly, the only source of dissolved oxygen was the system influent; reactor inlet DO values were, therefore, significantly reduced. A significant effluent DO value of greater than 4.0 mg/L was maintained throughout. It is unlikely, therefore, this had any impact on TCE transformation rate or extent. Significant amounts of DO were consumed when the mixed water from the feed mixing reservoir passed through the fluidized bed. The pH was relatively stable before and after the water passed the bed. This was due to the high dilution rate since the recycled effluent flow was more than six times of the influent flow rate (or reactor overflow rate). The influent concentrations of BTEX and TCE were calculated based on the overflow rate, BTEX-TCE mixture feed rate by the syringe pump, the mass ratio of benzene:toluene:xylynes:TCE (wt/wt), and the density of the BTEX-TCE mixture, by using the following equations:

$$S_b = 10^9 \, qgf_b / (60Q) \qquad \textbf{(6-1)}$$

$$S_t = 10^9 \, qgf_t / (60Q) \qquad \textbf{(6-2)}$$

$$S_x = 10^9 \, qgf_x / (60Q) \qquad \textbf{(6-3)}$$

and

$$S_{TCE} = 10^9 \, qgf_b / (60Q) \qquad \textbf{(6-4)}$$

where, S_b, S_t, S_x, and S_{TCE} are influent concentrations for benzene, toluene, xylenes and TCE (μg/L), respectively; f_b, f_t, f_x, and f_{TCE} are mass fraction of benzene, toluene, xylenes and TCE in the BTEX-TCE mixture (f_b = 0.2431, f_t=0.4907, f_x=0.2601, and f_{TCE}=0.00579 in this study); q is syringe pump feed rate for the BTEX-TCE mixture (0.150 ml/hr in this study); g is density of the BTEX-TCE mixture (0.8733 g/ml in this study); and Q is the effluent flow rate (ml/min).

Under these operational conditions, the average TCE removal was 70.0% at a volumetric rate of 1.82 mg/L-day. More than 99.9% of influent BTEX were removed at a volumetric BTEX removal rate of 1.4 Kg COD/m^3-d. The BTEX and toluene/TCE consumption ratios were ca. 247 and 121 mg/mg, respectively. Experimental results indicated that higher TCE removal efficiency was achieved by increasing the HRT, as predicted.

In Section 5.2, we estimated the TCE removal efficiency by the GAC-FBR is within an "attainable" region (performance curves of CSTR and PFR systems). The operational results obtained from this test supported this estimation. The value of TCE removal efficiency is obtained during this period was within the attainable region (Figure 5-1).

Table 6-1. Reactor performance at steady-state conditions with recirculation.

Days	217-233
Operational Conditions	
Temperature (°C)	20.1±0.4
HRT (min)	26.9±0.8
Overflow rate (ml/min)	261±07
pH	
feed reservoir*	6.1±0.1
effluent	6.0±0.3
DO concentration (mg/L)	
feed reservoir*	8.9±1.8
effluent	4.5±1.9
BTEX Removal	
Total BTEX	
influent (μg/L)**	8330±242
effluent (μg/L)	5.9±1.2
removal (%)	>99.9
Benzene	
influent (μg/L)**	2033±56
effluent (μg/L)	n.d.
Toluene	
influent (μg/L)**	4094±113
effluent (μg/L)	0.52±0.2
Xylenes	
influent (μg/L)**	2169±60
effluent (μg/L)	5.6±1.2
Total BTEX removal rate (mg/L bed-day)	447±18
TCE Removal	
TCE concentration	
influent (μg/L)**	48.3±1.4
effluent (μg/L)	14.5±1.3
removal (%)	70.0±2.6
TCE removal rate (mg/L bed-day)	1.82±0.07
BTEX/TCE consumption (mg/mg)	247±17
Toluene/TCE consumption (mg/mg)	121±4.9
*The samples for the DO and pH were taken from the feed mixing reservoir where the influent and recycled effluent were mixed together. **The influent concentrations were calculated.	

7. SUMMARY

- A GAC-FBR system was started-up for degradation of BTEX and TCE at ambient temperature conditions (21-22°C) with synthetic groundwater containing 190 μg TCE/L and 6000 μg BTEX/L. The hydraulic retention time (HRT) was 5.9 minutes during start-up. A stable biofilm was formed on the GAC carrier within 10 days with BTEX removal efficiency averaging greater than 99%. The presence of TCE in the influent did not inhibit the development of a biofilm or BTEX removal.
- Sustained, co-metabolic TCE transformation in the GAC-FBR system was verified by changing the amount of oxygen delivered to the reactor influent. No TCE removal occurred when influent DO was reduced to near zero. TCE removal was restored when oxygen was again added to the influent.
- Throughout this study, the reactor was loaded with the same mass ratio among benzene, toluene and xylenes (1:2:1 wt/wt). TCE degradation efficiency was examined at four different steady-state conditions with one-pass feed (5.6 minute HRT). Under all test conditions, with BTEX loading rates ranging from 1.87 to 4.1 Kg COD/m^3-d, BTEX removal efficiencies were greater than 99.9%; effluent BTEX concentrations were below detection limits.
- Under the first steady-state condition, the reactor was fed with a moderate TCE concentration (380 μg/L) with a BTEX/TCE loading ratio of 17/1 (mg/mg). Average TCE removal efficiency was 32.7% with a BTEX/TCE consumption ratio of 44.9 mg/mg.
- The second steady-state condition was designed to test TCE removal performance with increased BTEX/TCE loading ratio (37/1) and reduced TCE concentration (160 μg/L). An average TCE removal efficiency of 30.8% was achieved at a BTEX/TCE consumption ratio of 110.9 mg/mg. The results suggested that the increased BTEX/TCE loading ratio actually reduced TCE removal efficiency slightly.
- The third steady-state condition was designed to test TCE removal performance at a reduced BTEX/TCE loading ratio (17/1) and a TCE concentration of 180 μg/L. An average TCE removal efficiency of 36.3% was achieved with a BTEX/TCE consumption ratio of 41.8 mg/mg. The lower BTEX/TCE ratio increased TCE removal efficiency slightly.

- The fourth steady-state condition was designed to test TCE removal performance with a low influent TCE concentration (ca. 60 μg/L). The BTEX/TCE loading ratio was 50 mg/mg. An average TCE removal efficiency of 19.0% was achieved with a BTEX/TCE consumption ratio of 109 mg/mg at a somewhat reduced temperature (18°C).
- The results obtained from batch assays indicated that co-metabolic TCE degradation rate was inhibited in the presence of BTEX. The batch assays indicated that the biomass taken from upper portion of the fluidized bed had sufficient TCE degradation capability when BTEX/TCE and toluene/TCE consumption ratios were as low as 42 and 21 mg/mg, respectively. Co-metabolic TCE degradation appeared to follow first order reaction kinetics.
- The biomass from the GAC-FBR were capable of degrading TCE, *cis*-1,2-DCE, *trans*-1,2-DCE and vinyl chloride. The degradation rates for *cis*-1,2-DCE and VC, two major anaerobic metabolic intermediates of TCE, were almost three-fold higher than for TCE.
- Based on the results obtained from reactor operation and batch assays, TCE removal performance by the GAC-FBR with different HRT and influent TCE concentrations was estimated using kinetic analysis and modeling. Higher TCE removal efficiency can be achieved by increasing HRT.
- Higher TCE removal efficiency (70%) was, in fact, achieved with a longer HRT (26.9 min) when recirculation of reactor effluent was used. Results from this steady-state period confirmed the modeling estimates. Effluent TCE concentrations of <15 μg/L were achieved.

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SECTION 6 - EVALUATION OF THE APPLICATION OF THE GRANULAR ACTIVATED CARBON-FLUIDIZED BED REACTOR (GAC-FBR) FOR THE TREATMENT OF DINITROTOLUENE (DNT) AT THE RADFORD ARMY AMMUNITION PLANT (RAAP)

Evaluation of the Application of the Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) for the Treatment of Dinitrotoluene (DNT) at the Radford Army Ammunition Plant (RAAP)

Final Report

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Executive Summary

A field demonstration was conducted to examine the effectiveness of a commercial scale Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) for removal of dinitrotoluene (DNT) from water-dry wastewater generated during munitions manufacturing. The location for this demonstration was the Radford Army Ammunition Plant (RAAP). The system is intended for use as pretreatment to remove DNT present in water-dry wastewater at a low flow, high concentration point source prior to entering the RAAP wastewater treatment system. The demonstration included monitoring during eight operational periods each of which differs from the others in one or more key operational characteristics. The demonstration included installation and start-up, acclimation to water-dry wastewater, technical evaluation of reactor performance, decommissioning of the GAC-FBR, and design and economic analysis of a full scale GAC-FBR for the site. Throughout the entire project DNT removal efficiencies were greater than required to meet the plant effluent discharge limitations on RAAP's NPDES permit.

In June, 1994, an Envirex Model 30 GAC-FBR system was delivered to RAAP. The system was built to design specifications established by Michigan Biotechnology Institute. It was outfitted for anaerobic operations. The GAC-FBR was installed in early July. A programmable logic controller (PLC) was installed to monitor critical reactor parameters and to control key functions. The PLC also contained a series of interlocks designed to protect the reactor and biological system from damaging upsets, and was interfaced to an autodial system to alert on-call personnel to conditions requiring operator attention. The PLC was also interfaced to a computer and modem, which facilitated remote observation of current reactor conditions and downloading of stored performance data.

System performance assessment was based on analysis of the influent and effluent streams. The influent and effluent wastewater streams were analyzed for DNT, DAT, ethanol, ether, short chain fatty acids, and COD. Added to the influent wastewater was the measured flow of a supplemental ethanol/sucrose stream used to adjust the COD loading rate to the reactor independent of the DNT loading rate. The effluent gas stream was directly measured using a wet test gas meter and analyzed using an in-line infra-red gas analyzer. The methane concentration in the effluent wastewater was determined from the gas phase methane concentration using Henry's Law. The concept of "usable COD" (i.e. COD that could be readily used by the anaerobic microbial consortia in the GAC-FBR system) was used as a measure of the primary substrate and thus of available reducing power.

Throughout the demonstration, when sufficient primary substrate was present, the anaerobic GAC-FBR system removed DNT to within the facility discharge limits for RAAP. The net average effluent DNT level throughout the course of the demonstration was 0.03 mg/L vs. a facility discharge average limit of 0.113 mg/L. Even when there was insufficient primary substrate present during one period, the effluent DNT only reached 0.6 mg/L (>99% removal), a level which would not cause the facility discharge limit to be exceeded.

During the course of this work, the limited availability of water-dry wastewater prevented increasing the DNT loading rate beyond the capability of the GAC-FBR system. The maximum applied DNT loading rate, and thus the minimum equipment size required and operating costs could not, therefore, be identified.

During the eight operational periods, the applied DNT loading rate was varied from 370 to 1390 g DNT/m^3-d. The usable COD:DNT ratio was varied from a high of 18.1 during the first period

(initial operation) to a low of 1.2 during the forth period, and then up in several steps to 13.9 in the final period. DNT removal efficiencies were above 99.95% and DNT effluent levels were below the permitted plant discharge levels for all ratios of 2.1 or higher. A ratio of 3 was conservatively selected for the economic analysis.

In six of the eight operational periods, the mass balance on usable COD generally gave an excellent accounting of recovery of influent usable COD between DNT reduction, methane generation, biomass production, and effluent usable COD. Results from the first and last periods gave a slight under-accounting. These periods both had a high driving force for biomass accumulation that could account for the observed results.

GAC from the reactor was sampled several times during the course of the study and analyzed for adsorbed DNT and DAT. No DNT was recovered from any of the samples. This confirmed that the complete transformation of DNT to DAT and other reduced species occurred. DAT was observed in all GAC samples taken from 4/17/95 on. The measured DAT on the GAC samples was directionally less than the amount calculated from measured throughput and influent and effluent analyses. This is consistent with a combination of irreversible adsorption onto the GAC, polymerization of a portion of the adsorbed DNT, and less than full recovery of DAT from the trapping resin in the thermal analysis method used herein.

The GAC-FBR system was decommissioned in August, 1995, and prepared for movement to another site. The reactor system was thoroughly cleaned by recirculating a caustic solution overnight. After neutralization, the cleaning solution was discharged to RAAP's wastewater treatment plant.

The design criteria for economic analysis was based on a production level of 4.0 million pounds of DNT containing propellant per year, their estimated production level for the next five years. The design treatment rate of 4 gpm is the maximum generation rate that would result from simultaneous use of all eight currently active water-dry buildings on an 11 day cycle. At this rate, the annual production would be completed in less than half of the year. The design influent concentrations for DNT and usable COD were based on the analysis of results during the longest period of sustained operation during this demonstration.

The GAC-FBR system recommended for installation at RAAP is a Model 190 system which has a working bed capacity of 5.2 m^3 working bed volume. The Model 190 is the next standard size up from the Model 30 utilized for this demonstration. Based on the maximum DNT loading rate successfully demonstrated during this project, the Model 190 has the capacity to treat 7.2 Kg DNT/d, 85% over the design criteria. In continuous use, this system has the capability to successfully treat RAAP's DNT containing water-dry wastewater even if production requirements quadrupled.

The capitol cost for the anaerobic GAC-FBR was estimated at $225,000. The total operating and maintenance (O&M) cost, less labor, was estimated at $2,940 per year, over half of which is for electrical power. The rental liquid phase GAC adsorption system currently in use at RAAP had an initial setup cost of $5,360, an annual rental cost of $22,500, and a change-out service charge of $5,710 per event. At the design loading rate, there would be 16.5 changeout services required at an annual cost of $94,215. The total O&M cost for the GAC adsorption system is thus $122,075. The high O&M costs for GAC adsorption offset the GAC-FBR's higher initial cost in less than two years. Assuming a 7% interest rate and a 20 year useful life, the annualized cost for the GAC-FBR system is $24,180, which is only 21% of the $117,221 annualized cost for the GAC adsorption system.

1 Background

Dinitrotoluene (DNT) is a contaminant present in wastewaters generated during the production and curing of propellants. It enters the wastewater stream through several operations but the major contributor is water-dry operations. In this process, the propellant is steeped in hot water to remove solvents, primarily ethanol and diethyl ether. The water-dry wastewater becomes essentially saturated with DNT as well as containing varying levels of ethanol and ether.

DNT is a suspected carcinogen, and is toxic to aquatic life forms. The effluent discharge for DNT set in the NPDES permit for the Radford Army Ammunition Plant (RAAP) effluent is 113 µg/L average and 285 µg/L maximum. RAAP has been cited for exceeding this level in their plant discharge, which feeds into the New River at the Plant's boundary.

As with many of the nitrated aromatic compounds found in effluents from ammunition production, DNT is not consistently removed to these low levels in conventional biological treatment processes such as the rotating biological contactors (RBCs) used at RAAP or activated sludge processes common for municipal and industrial wastewater treatment. The predominant method utilized for removal of DNT from wastewater is adsorption on granular activated carbon (GAC) with subsequent incineration of the GAC.

Previous work supported by CERL has shown that DNT can be stoichiometrically reduced to DAT under methanogenic conditions if there is a primary growth substrate present. Ethanol, a co-contaminant in the water-dry wastewater, is an appropriate primary substrate. The DAT thus formed is resistant to further anaerobic transformation but is readily mineralized under aerobic conditions such as present in the RBC's at RAAP.

Additional work supported by CERL has shown that at the bench scale, DNT can be anaerobically reduced to DAT in an anaerobic granular activated carbon fluidized bed reactor (GAC-FBR). This reactor offers the advantages of both biological and conventional adsorptive treatment. The GAC serves as a support surface for the anaerobic bacteria, offering very high surface areas and thus high specific biomass levels in compact reactor systems. The GAC also serves as an adsorbent during start-up or peak loads, when the DNT concentration is temporarily higher than the capacity of the bacterial population to reduce DNT, or when there is a lack of sufficient primary substrate to provide sufficient reducing power for complete transformation of all of the DNT to DAT. In these cases, the DNT is adsorbed and held for subsequent desorption and biodegradation when the DNT concentration decreases.

Based on successful bench-scale work, this field demonstration was initiated to treat DNT containing water-dry wastewater at RAAP. In a separate but related study, the effluent from the anaerobic GAC-FBR was treated aerobically in a small pilot RBC, to demonstrate an integrated anaerobic-aerobic biological treatment process for complete mineralization of DNT.

2 Design and Procurement of a Commercial Scale GAC-FBR for Feasibility Demonstration

2.1 Design Criteria

An anaerobic GAC-FBR, built by Envirex, Inc. to the design specifications established by Michigan Biotechnology Institute, was used for this demonstration project. The stainless steel reactor shell had a 50.8 cm (20 inch) diameter and a total height of 4.42 meters (14.5 feet). The GAC-FBR had a maximum working volume of 0.71 m^3. The reactor was filled with ca. 350 pounds of GAC (Calgon MRX-P 10X30). The GAC was maintained in a fluidized state by the constant upward flow of 30 gallons of combined influent and recycled effluent. The reactor was wrapped with an insulating blanket to maintain the design operating temperature of 35°C.

Influent was fed through a variable speed positive displacement pump. A constant hydraulic flux through the reactor was maintained using a duplex fluidization pump system (one active, one spare). The fluidization pump delivered a mixture of system influent and treated effluent (recycle) at a constant flow rate, regardless of the influent flow rate. Provision for delivery of a supplemental ethanol/sucrose/water mixture was added. This supplemental feed was initially added at a port just prior to the inlet basket strainers, but subsequently directed into the reactor feed line on the discharge side of the fluidization pump. A small diaphragm pump was used to supply necessary major and trace nutrients to the system. Effluent pH was controlled by addition of a NaOH solution to the reactor influent through a variable speed diaphragm pump.

Effluent water flowed to a separator chamber which captured any GAC in the effluent. The effluent then overflowed from the separator to other unit treatment operations not included in this phase of the study. A separate line, exiting from a lower point on the separator, provided water to the fluidization pump for recycle. Periodically, a pump drew water from the bottom of the separator and from the biomass control point on the reactor and returned the entire flow to a point below the reactor bed height control point. This process sheared excess attached biomass from the GAC and then returned the GAC to the reactor. The biomass control point was located at a bed height of 3.5 meters (11.5 feet) yielding a maximum working bed volume of 0.71 m^3. Hydraulic residence times are based on this maximum volume. The sheared biomass was carried out of the reactor in the effluent flow. The separator tank was fitted with a heating element. A temperature sensor used to control the heating element was mounted in the recycle line.

A small stream of effluent water was pumped back up to the top of the reactor and sprayed on the free water surface to control any foaming that may have occurred.

Gas generated in the reactor was routed through a wet test gas meter (WTGM) for volume measurement and then vented to the atmosphere outside the test building (see Section 2.3.)

A programmable logic controller (PLC) was used to monitor critical reactor parameters and control key functions such as effluent pH and temperature. The PLC also contained a series of interlocks designed to switch the reactor to warm (full recycle) or cold (total) shutdown in the event of out of limits operations. This was to protect the reactor and biological system from damaging upsets. The PLC also stored operational data for detailed evaluation. A summary of the data set, in hourly increments, is included on computer disk, in Microsoft Excel format.

2.2 Utilities Requirements

The GAC-FBR system, as provided, was skid-mounted and essentially self contained. It required a 30 amp, 460 volt, three phase power supply. Influent and effluent lines were connected through flanges that could be adapted to any common fitting required. The effluent gas line from the WTGM was flexible tubing. This line must be vented to an outside location where methane gas will not accumulate.

2.3 Gas Analysis Equipment

The reactor system was outfitted with optional equipment for monitoring the effluent gas. This included the WTGM mentioned in Section 2.1 for measuring total gas production. In addition, a portion of the effluent gas was drawn through a compressed air powered gas conditioner (dehumidifier) into an infra-red gas analyzer (IRGA). Exhaust gas from the IRGA was returned to the effluent gas line for volume measurement by the WTGM. The IRGA provided a continuous readout of the methane and carbon dioxide concentration in the effluent gas. This data was also transmitted to the PLC for storage along with other key system parameters.

2.4 Telemetric Package

The PLC was interfaced to a telemetric package that provided remote access via computer modem. This package allowed remote observation of current reactor conditions in addition to downloading of all stored data. During the course of this project, data was routinely downloaded and evaluated by MBI/EFX personnel in Lansing, MI.

The PLC was also connected with an autodial/autoalarm system that alerted on-call personnel to warm or cold shutdown conditions.

3 Installation and Start-up of the GAC-FBR

3.1 Installation of the GAC-FBR

The anaerobic GAC-FBR system was shipped to RAAP in late June, 1994, and installed on site in early July. Hercules (AlliantTechSystems) personnel/contractors moved the reactor column and support skid into place and provided rigging support for installation of the heavier components. Personnel from Envirex and MBI provided on-site assistance during the installation.

Once assembled, the pH and DO probes were calibrated. The reactor was filled with clean water and charged with 350 pounds of GAC (Calgon MRX-P 10X30). The pH was adjusted to 6.8. Liquid fluidized beds are by nature classifiers. Small and light particles will segregate towards the top of the fluidized bed. After the GAC was fluidized for about 2 hours, the top one foot of the bed was siphoned off and discarded to remove carbon fines. The pressure at the base of the reactor was then measured at flow rates ranging from 20 to 40 gpm. Changes in the reactor inlet pressure are carefully monitored to ensure there is no plugging of the liquid distribution system at the base of the reactor.

3.2 Initial GAC-FBR Start-up

The GAC-FBR was started up on 9/12/94. Biological inoculation was performed over a 3-day period, on 9/13, 9/14, and 9/15. On each date, a combination of biomass coated GAC and suspended biomass cultures were added to the reactor, and the system was operated on full recycle overnight. The "seeded" GAC was harvested from MBI pilot-scale reactors anaerobically treating a synthetic DNT wastewater and a brewery wastewater. The suspended biomass inocula included sludge from the DNT pilot-scale reactor effluent and biomass removed a pilot-scale reactor treating brewery waste.

The initial feed to the anaerobic reactor at RAAP was a mixture of 2-T ethanol and water, fed at 0.3 gpm. The 2-T ethanol is ethanol denatured by the addition of 2% toluene. This feed provided an applied organic loading rate (OLR) of 5 Kg COD/m^3-d. (The volumetric measure for the OLR is the volume of the mature expanded bed.)

3.3 Re-inoculation of the GAC-FBR System

Over the first six weeks of operation, numerous operational difficulties were experienced. These included several cold shut-downs, high (>9) and low (<6.0) pH excursions, inadequate temperature control, and organic overloading of ethanol during a period when the system was on complete recycle. The causes and corrective actions for these problems are detailed later in this section. Due to concerns that the biomass from the original inocula fed into the system may have been inhibited or killed-off during these operational difficulties, it was decided to reinoculate.

On 11/3, 11/5, and 11/7, the reactor was inoculated with anaerobic sludge from the primary and secondary digestors at the Pepper's Ferry Wastewater Treatment Plant. Each day's inocula totaled about 8 gallons. After each addition, the reactor was operated in total recycle (no influent flow) overnight to allow sufficient time for attachment of the inocula to the GAC.

To ensure rapid biomass growth on the GAC, the reactor was fed a sugar (sucrose) solution at an applied OLR of 5 Kg COD/m^3-d for a one week period. For the second and third weeks following the reinoculation, the feed was changed to a 50:50 mixture (on a COD basis) of sugar and ethanol.

The applied OLR was maintained at 5 Kg COD/m^3-d. On 11/25, the feed composition was again changed to provide 90% of the COD as ethanol and 10% as sugar. The OLR was held constant.

On 12/28, the OLR was increased to 7 Kg COD/m^3-d, using the 90:10 mixture of ethanol/sucrose. On 1/3/95, the applied OLR was further increased to 10 Kg COD/m^3-d. The reactor was operated at this OLR for four weeks, while awaiting availability of DNT containing water-dry wastewater.

3.4 Operational Start-up Difficulties Encountered and Corrective Actions Taken

3.4.1 Temperature Control

The reactor was supplied with a 3 KW heater mounted in the separator tank, controlled by the PLC. This heater was subsequently found to be insufficient to maintain the desired operating temperature of 35°C. A supplemental 5 KW heater was installed on the influent line upstream of the influent pump on December 14, 1994. This heater was controlled by an integral thermostat. This additional heating capacity allowed the reactor temperature to be easily maintained at 35°C throughout the winter months.

Shortly after the new heater was installed, however, a problem was noted with the influent transfer pump losing prime. This flexible impeller pump is cooled by flow of water through the pump. The loss of prime resulted in the pump becoming overheated, eventually resulting in destruction of the impeller. The problem was traced to off-gassing of dissolved gases in the influent flow due to the significant temperature rise in the heater. An in-line gas separator was subsequently installed between the heater and pump, eliminating this problem.

3.4.2 Gas Production Measurement

The WTGM counter on the control panel was observed to read improperly. The problem was traced to the PLC, which was using the same register for recording counts on the WTGM and the low pH control tank alarm value. The PLC was reprogrammed by Envirex to correct this problem. In addition, the WTGM was occasionally observed to run backwards. This was generally observed to be associated with hydraulic surging (discussed in Section 3.4.5 below) and with hydrostatic pressure changes associated with recycle of GAC from the separator to the reactor column during periods of low reactor loading (and thus low gas production rates).

3.4.3 Supplemental Ethanol/Sucrose Addition Point

The ethanol and sucrose solution was initially added to the influent line prior to the duplex basket strainer. Significant biological growth was noted in the strainer baskets and lines leading to the point at which this stream was mixed with the recycle stream (suction side of the fluidization pump). The problem was traced to the availability of easily metabolized COD coupled with the low influent flow rates. The problem was corrected by relocation of the supplemental feed addition point to the discharge side of the fluidization pump.

3.4.4 PLC Computer Operation/Logic

Several problems were encountered with the ladder logic programmed on the PLC. These were identified during initial operations and subsequently corrected. The corrective actions taken are as follows:

- Alarms and interlocks for low levels in the nutrient and pH control media tanks were eliminated;
- An interlock was added to stop the nutrient and supplemental ethanol pumps when the system switches to bypass;
- The counts for the WTGM, originally routed to a register shared with the low pH control media tank level alarm, were routed to a dedicated register;
- The reset criteria for low pH excursions was changed to require raising the pH to within limits and pushing a reset button;
- The low pH alarm was interlocked to close the bypass valve and stop the nutrients pump;
- The low reactor flow alarm was interlocked to disable the heater;
- The low influent flow alarm interlock was modified to disable the nutrient and supplemental ethanol pumps, and not disable the pH control pump;
- The low-low and high-high temperature alarm limits were changed from preset (imbedded) to user definable;
- and, a user selectable switch was added to enable or disable the low influent flow alarm.

The computer was removed from the system and shipped to Envirex for reprogramming to accomplish the above changes. In addition, the computer system was modified to enable reprogramming of the PLC via remote modem access.

3.4.5 Effluent Surging

The effluent flow rate was observed to surge, causing significant variation in the water level in the separator and reactor proper. This resulted in difficulties in accurately measuring gas production rates. The problem was corrected by addition of a vacuum break at the top of the inverted U in the effluent downcomer line.

3.4.6 Infra-Red Gas Analyzer (IRGA) Calibration

The IRGA analysis for both methane and carbon dioxide was observed to drift upwards until it went out of scale. Automatic internal rezeroing required exceptionally long time intervals, and resulted in the start of another upward drift. Normal recalibration checks read within limits, but on leaving the IRGA in calibration mode, the same upward drift was observed. The IRGA was returned to the factory for repair. Upon return, it functioned properly.

4 Measurements, Analyses and Methods of Performance Evaluation

Performance of any treatment system is normally based on analysis of influent and effluent streams. In this demonstration, the influent stream had two components, the influent water dry wastewater and a supplemental ethanol/sucrose feed solution. Samples of the influent to the GAC-FBR were obtained from a sampling port just after the influent basket strainers. Initially, this permitted sampling and analysis of the influent after addition of any ethanol and/or ethanol/sucrose mixture required to obtain the desired applied OLR. When the addition point of the supplemental ethanol (or ethanol/sucrose) feed was moved to the discharge side of the fluidization pump, it was not possible to obtain a representative sample of the actual influent to the system. Therefore, analytical results for the system influent are for the raw wastewater and do not reflect the contribution of the added organics. The feed rate of the supplemental organic feed solution was measured daily. By adding the amount of this known COD input to the measured amount in the raw wastewater, it is possible to calculate the actual influent concentration of ethanol and COD. This was done in assessing system performance.

When analyzing the performance of the GAC-FBR system, the concept of "usable COD" as a measure of the primary substrate that was available under anaerobic conditions and thus available reducing power was used. Only that portion of COD available from ethanol and the volatile fatty acids (acetate and propionate) was observed to be available to provide reducing power for the conversion of DNT to DAT. Other COD including that from DNT, DAT and ether was not included in this analysis. DNT was not degraded but rather was only transformed (reduced) to DAT. Ether was observed to be essentially inert, passing through the system without being degraded or transformed.

For example, on January 31, 1995 the wastewater feed to the GAC-FBR system contained 144 mg/L ethanol, 53 mg/L acetate, no measurable propionate, and 763 mg/L COD. The supplemental ethanol-provided an additional 1022 mg/L ethanol to the inlet wastewater. The calculated influent, therefore, had a total of 1166 mg/L ethanol and 2,889 mg/L COD (2,216 mg/L from the supplemental ethanol). The usable COD was 2,482 mg/L comprised of 2,425 mg/L from the total influent ethanol plus 57 mg/L from the acetate in the influent. There was no propionate in the influent in this case.

As part of the performance analysis, a mass balance was made on usable COD for each operational period. Influent usable COD was calculated as described above. The COD contributions of ethanol, acetate, and propionate in the effluent constitute that portion of usable COD which was not utilized in the system. The usable COD utilized for reduction of DNT to DAT was calculated from the net change in DNT concentration times the COD difference between DNT and DAT. This assumes that all of the DNT removed was transformed to DAT. This assumes that no adsorption of DNT occurred (i.e. there was equilibrium between the DNT in the aqueous phase and the GAC biomass carrier). This is probably not true for all performance periods examined. (See Chapter 5.) The calculation for the mass of methane generated included methane exiting the system in both the gaseous and liquid (dissolved) phases. Methane in the gas phase effluent was calculated using the gas production (measured using the WTGM) times the methane concentration measured by the in-line IRGA. The liquid phase effluent was calculated using the equilibrium liquid phase concentration, based on the measured gas phase concentration using Henry's Law. It was assumed that 15% of the consumed usable COD was utilized for cell growth. This is about 90% of the maximum yield determined for anaerobic metabolism of short chain alcohols (McCarty, 1974). During periods immediately after significant changes in the applied OLR, there would be a strong driving force for

change in biomass levels in the system. This could result in an under (or over) estimate of the fraction of available energy being directed to cell synthesis.

5 Results

5.1 Overview of Performance

Throughout the demonstration, when sufficient primary substrate was present, the anaerobic GAC-FBR system removed DNT to within the discharge limits for RAAP. The net average effluent DNT level throughout the course of the demonstration (76 individual analyses) was 0.03 mg/L vs. an average limit of 0.113 mg/L. Even when there was insufficient primary substrate present during one period, the DNT level in the GAC-FBR effluent only once exceeded the individual sample limit for plant effluent of 0.285 mg/L, with a concentration of 0.6 mg/L. Even this level would not cause the final plant discharge to exceed the NPDES limit due to the low flow rate of this point source. The time course of influent and effluent DNT is presented in Figure 5-1. The analytical data are listed in Appendix B.

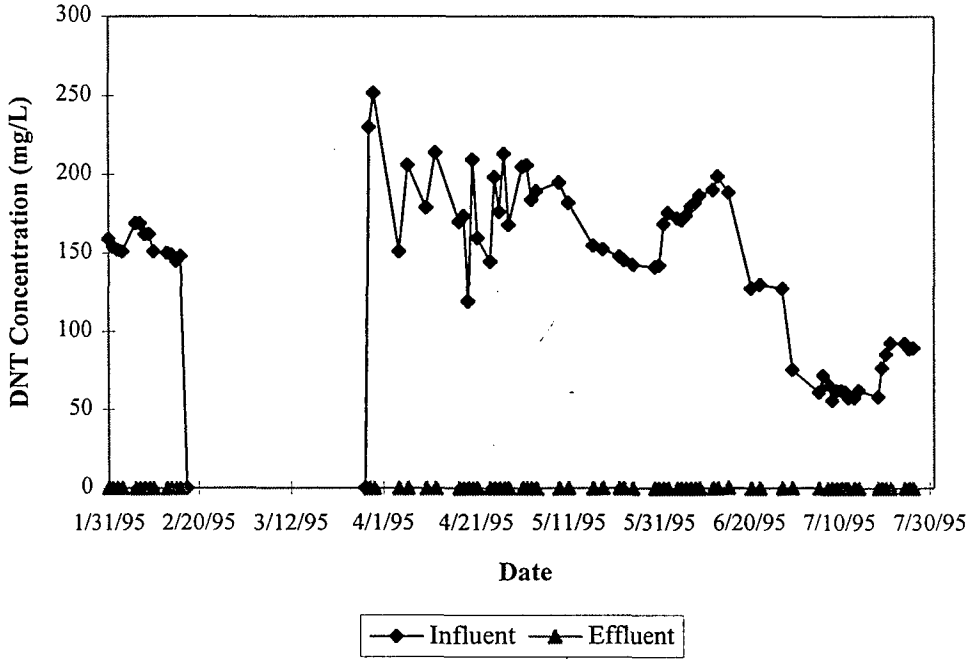

Figure 5-1. DNT Influent and Effluent Timecourse

The performance of the GAC-FBR was evaluated during eight operational periods, each of which differs from the others in one or more key operational characteristics. In aggregate they offer insight into operational requirements for insurance of good performance. During the course of this work, time constraints and limited availability of the water-dry wastewater prevented increasing the DNT loading rate beyond the capacity of the GAC-FBR system. The upper limit of performance, and thus the minimum equipment size required and operating costs could not, therefore, be identified.

5.2 Initial Operation and Acclimation to DNT-Containing Wastewaters

Water-dry wastewater (DNT, ethanol and ether the primary contaminants) first became available in late January 1995. At this time, the GAC-FBR was operating on a 90:10 mixture of ethanol and sucrose (COD basis) at an OLR of 10 Kg COD/m^3-d. Beginning on 1/30/95, DNT wastewater was fed to the reactor at 0.4 gpm. The supplemental ethanol/sucrose solution feed rate was decreased to maintain the same total OLR. On February 11th, the supplemental feed stream was converted to ethanol while maintaining the same applied OLR. The initial supply of DNT containing

wastewater was exhausted on February 16th. Performance during this initial period is discussed in Section 5.3.1.

DNT containing water-dry wastewater was not available again until March 28th. The reactor was continually operated at a 10 Kg COD/m^3-d OLR in the interim using ethanol as the sole added organic substrate. There was essentially a continuous supply of DNT wastewater from March 28th through the end of this project in late July 1995.

5.3 Evaluation of Performance During Different Operational Periods

5.3.1 Operational Period #1 (1/31/95 to 2/16/95)

Approximately two weeks after starting flow of the water dry production wastewater to the GAC-FBR reactor, the system performance was intensively monitored for a two week period. A summary of results for this period is presented as Table 5-1. The forward feed rate to the reactor was 0.4 gpm, yielding an empty bed hydraulic residence time of 7.8 hours. The feed was supplemented with ethanol, to provide an additional 2460 mg COD/L to the influent. The supplemental ethanol comprised ca. 75% of the total applied COD load and provided 88% of the usable COD during this period. The applied OLR during this period averaged 10 Kg COD/m^3-d while the usable applied OLR was 8.6 Kg COD/m^3-d.

Table 5-1. Performance Summary for Operational Period No. 1

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
1/31/95	159	0.111	488	99.93%	1166	584	53	786	bdl	7.8	2920	2100	9.0
2/1/95	154	0.11	473	99.93%	1197	567	47	817	bdl	8	2963	2138	9.1
2/2/95	152	0.117	467	99.92%	1276	445	52	768	bdl	6.7	3137	1888	9.7
2/3/95	151	0.113	464	99.93%	1290	464	47	922	bdl	8.2	3180	1950	9.8
2/6/95	169	0.03	519	99.99%	1063	152	55	1031	bdl	14.9	2720	1325	8.4
2/7/95	169	0.03	519	99.99%	1121	263	54	852	bdl	7.2	2856	1375	8.8
2/9/95	162	<0.02	497	>99.99%	981	143	49	670	bdl	2.1	2514	1025	7.8
2/10/95	151	0.006	464	99.99%	1572	675	48	678	bdl	bdl	3768	1700	11.6
2/13/95	150	<0.006	461	>99.99%	1581	672	56	652	bdl	bdl	3776	1800	11.6
2/14/95	149	0.006	458	99.99%	1607	690	55	648	bdl	bdl	3832	2125	11.8
2/15/95	145	0.008	445	99.99%	1293	739	54	690	bdl	bdl	3177	2200	9.8
2/16/95	148	0.01	454	99.99%	1692	919	55	574	bdl	bdl	4006	2450	12.3
Average	155	0.04	476	99.97%	1320	526	52	757	bdl	4.6	3239	1840	10.0

Influent DNT concentration averaged 155 mg/L yielding an applied DNT loading rate of 476 g DNT/m^3-d. Effluent DNT concentrations for the first four days of the period averaged 0.113 mg/L; effluent DNT was below detection limits for seven of the remaining eight sampling days, averaging 0.047 mg/L for the entire operational period. The average removal efficiency for DNT was 99.97%. Forty percent of the influent ethanol was unreacted, indicating that there was insufficient biomass in the GAC-FBR system at this point in time to complete ethanol oxidation. The effluent acetate concentration averaged 760 mg/L, indicating that there was also an insufficient acetate metabolizing methanogenic population present. The methane produced was primarily the result of H_2 (produced during anaerobic ethanol oxidation) conversion.

A mass balance of usable COD is presented as Table 5-2. Results for this operational period indicated that 31% of the usable COD in the influent was consumed in the reactor. The remaining 69% was discharged in the effluent, primarily as acetate and ethanol. Based on measured DNT disappearance and methane production, 3% of the influent usable COD was used for DNT reduction and 11% went to methane production. Assuming 15% of the usable COD consumed was utilized for cell growth, a total of 87% of the usable COD is accounted for. With the high level of ethanol

available, the proportion of usable COD utilized for cell growth was probably higher than 15% during this period, bringing the mass balance even closer to closure.

Table 5-2. Usable COD Balance for Operational Period No. 1

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
1/31/95	2482	2075	407	7.6	84	216	61	84%	3%	9%	2%	98%
2/1/95	2540	2074	466	7.8	82	442	70	82%	3%	17%	3%	105%
2/2/95	2710	1765	945	8.3	80	118	142	65%	3%	4%	5%	78%
2/3/95	2734	1973	761	8.4	80	171	114	72%	3%	6%	4%	86%
2/6/95	2271	1452	819	7.0	90	431	123	64%	4%	19%	5%	92%
2/7/95	2390	1478	912	7.3	90	189	137	62%	4%	8%	6%	79%
2/9/95	2093	1024	1068	6.4	86	577	160	49%	4%	28%	8%	88%
2/10/95	3322	2136	1186	10.2	80	153	178	64%	2%	5%	5%	77%
2/13/95	3349	2102	1247	10.3	80	363	187	63%	2%	11%	6%	82%
2/14/95	3401	2135	1266	10.4	79	351	190	63%	2%	10%	6%	81%
2/15/95	2748	2282	465	8.4	77	350	70	83%	3%	13%	3%	101%
2/16/95	3579	2531	1048	11.0	78	211	157	71%	2%	6%	4%	83%
Average	2802	1919	882	8.6	82	298	132	69%	3%	11%	5%	87%

5.3.2 *Operational Period #2 (4/17/95 to 4/28/95)*

During the second operational period, the supplemental ethanol rate was reduced to 242 mg/L. The forward feed rate to the reactor was maintained at 0.4 gpm, yielding an empty bed hydraulic residence time (HRT) of 7.8 hours. A summary of results for this period is presented as Table 5-3.

Table 5-3. Performance Summary for Operational Period No. 2

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
4/17/95	169.9	<0.05	522	>99.97%	493	bdl	20	488	bdl	bdl	1653	707	5.1
4/18/95	173.7	<0.05	533	>99.97%	251	bdl	19	304	bdl	bdl	1149	557	3.6
4/19/95	119	<0.05	365	>99.96%	413	bdl	18	584	bdl	2	1358	823	4.2
4/20/95	209.4	<0.05	643	>99.98%	569	15	26	676	bdl	bdl	1874	911	5.8
4/21/95	159.5	<0.05	490	>99.97%	485	bdl	25	557	bdl	6.3	1624	842	5.0
4/24/95	144.58	<0.05	444	>99.97%	248	bdl	24	259	bdl	2	1084	576	3.4
4/25/95	198.3	<0.05	609	>99.98%	589	20	22	567	bdl	bdl	1874	962	5.8
4/26/95	176.3	<0.05	541	>99.97%	639	45	24	624	bdl	bdl	1948	1023	6.0
4/27/95	213	<0.05	654	>99.98%	621	47	24	620	bdl	bdl	1980	1047	6.1
4/28/95	168.01	<0.05	516	>99.97%	602	36	25	611	bdl	2	1871	1028	5.8
Average	173	<0.05	532	>99.97%	491	16	23	529	bdl	1.2	1641	848	5.1

During this period, influent DNT concentration averaged 173 mg/L yielding an applied DNT loading rate of 532 g DNT/m^3-d, slightly higher than for the first operational period. Effluent DNT concentrations were below detection limits (<0.05 mg/L) for the entire operational period. The average removal efficiency for DNT was >99.97%. Ninety seven percent of the influent ethanol was transformed by the biomass, indicating a significant increase in the amount of biomass in the system since the first period. The effluent acetate concentration averaged 530 mg/L, indicating that there was still an insufficient acetate metabolizing methanogenic population present for complete conversion of ethanol to methane.

The mass balance of usable COD is presented as Table 5-4. Results for this operational period indicated that 42 % of the usable COD was consumed in the reactor, with the remaining 58% discharged in the effluent, primarily as acetate. Of the portion consumed, 9% was used for DNT

reduction and 26% went to methane production. A 15% allowance for COD utilization for synthesis of biomass brings the mass balance within 1% of closure.

Table 5-4. Usable COD Balance for Operational Period No. 2

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
4/17/95	1048	527	521	3.2	90	380	78	50%	9%	36%	7%	103%
4/18/95	543	328	214	1.7	92	226	32	61%	17%	42%	6%	125%
4/19/95	879	634	245	2.7	63	292	37	72%	7%	33%	4%	117%
4/20/95	1212	761	451	3.7	111	296	68	63%	9%	24%	6%	102%
4/21/95	1035	611	424	3.2	85	489	64	59%	8%	47%	6%	121%
4/24/95	542	283	259	1.7	77	190	39	52%	14%	35%	7%	109%
4/25/95	1248	654	594	3.8	105	318	89	52%	8%	25%	7%	93%
4/26/95	1355	768	587	4.2	93	277	88	57%	7%	20%	7%	90%
4/27/95	1317	767	550	4.0	113	118	83	58%	9%	9%	6%	82%
4/28/95	1279	738	541	3.9	89	118	81	58%	7%	9%	6%	80%
Average	1046	607	439	3.2	92	270	66	58%	9%	26%	6%	99%

5.3.3 Operational Period #3 95/30/95 to 6/7/95)

During the third operational period, no supplemental ethanol was added to the water dry wastewater. The ethanol concentration in the water-dry wastewater averaged 150 mg/L. The forward feed rate to the reactor was maintained at 0.4 gpm, for a 7.8 hour HRT. A summary of results for this period is presented as Table 5-5.

Table 5-5. Performance Summary for Operational Period No. 3

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
5/30/95	141	<0.05	433	>99.96%	159	bdl	32	41	2	bdl	738	379	1.7
5/31/95	142	<0.05	436	>99.96%	162	bdl	32	37	bdl	bdl	750	418	1.7
6/1/95	168.46	<0.05	517	>99.96%	150	bdl	33	40	bdl	bdl	765	414	1.6
6/2/95	175.7	<0.05	540	>99.96%	146	bdl	32	31	bdl	bdl	775	380	1.6
6/4/95	172.2	<0.05	529	>99.96%	152	bdl	30	21	bdl	bdl	777	367	1.6
6/5/95	171	<0.05	525	>99.96%	152	bdl	28	18	bdl	bdl	776	394	1.6
6/6/95	174	<0.05	534	>99.96%	148	bdl	25	14	bdl	bdl	761	369	1.5
6/7/95	179.8	0.097	552	99.95%	129	bdl	27	7	bdl	bdl	738	394	1.3
Average	166	<0.06	508	>99.96%	150	bdl	30	26	0.25	bdl	760	389	1.6

Influent DNT concentration averaged 166 mg/L yielding an applied DNT loading rate of 508 g DNT/m^3-d, near the average of the earlier operational periods. Effluent DNT concentrations were below detection limits (<0.05 mg/L) for seven of the eight analyses during the period. The average removal efficiency for DNT was >99.96%. The concentration of ethanol in the effluent was below detection limits. The effluent acetate concentration dropped to an average of 26 mg/L, indicating significant growth of the acetate metabolizing methanogenic population.

The mass balance of usable COD during this period is presented as Table 5-6. Results for this operational period indicated that 92 % of the usable COD was consumed in the reactor. Of the portion consumed, 25% was used for DNT reduction and 88% went to methane production. With a 15% COD utilization allowance for cell growth, the mass balance indicates 31% more usable COD can be accounted for than was added to the system. This discrepancy can probably be attributed to some adsorption of DNT and/or endogenous respiration during this period of low primary substrate feed concentrations.

Table 5-6. Usable COD Balance for Operational Period No. 3

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
5/30/95	368	44	324	1.1	75	247	49	12%	20%	67%	13%	113%
5/31/95	372	40	332	1.1	75	354	50	11%	20%	95%	13%	140%
6/1/95	348	43	304	1.1	89	297	46	12%	26%	85%	13%	137%
6/2/95	338	33	305	1.0	93	190	46	10%	28%	56%	14%	107%
6/4/95	349	23		1.1	91			7%	26%	0%	0%	33%
6/5/95	346	19	327	1.1	91	232	49	6%	26%	67%	14%	113%
6/6/95	335	15	320	1.0	92	396	48	5%	28%	118%	14%	165%
6/7/95	297	8	290	0.9	95	293	43	3%	32%	98%	15%	148%
Average	344	28	316	1.1	88	287	47	8%	25%	83%	14%	131%

5.3.4 *Operational Period #4 (6/8/95 to 6/15/95)*

During the fourth operational period, the forward feed rate to the reactor was doubled to 0.8 gpm, yielding an empty bed HRT of 3.9 hours. The water dry wastewater was not supplemented with ethanol during this period. A summary of results for this period is presented as Table 5-7.

Table 5-7. Performance Summary for Operational Period No. 4

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
6/8/95	182	0.064	1118	99.96%	138	bdl	31	34	bdl	bdl	777	396	3.1
6/9/95	186.6	0.11	1146	99.94%	114	bdl	31	16	bdl	bdl	733	385	2.6
6/12/95	190.36	0.198	1169	99.90%	68	bdl	39	0	bdl	bdl	644	384	1.9
6/13/95	198.89	0.119	1221	99.94%	69	bdl	33	0	bdl	bdl	655	415	1.9
6/15/95	188.64	0.6	1158	99.68%	66	bdl	28	0	bdl	bdl	628	410	1.9
Average	189	0.16	1163	99.88%	91	bdl	32	10	bdl	bdl	688	398	2.3

Influent DNT concentration averaged 189 mg/L yielding an applied DNT loading rate of 1163 g DNT/m^3-d, approximately twice the DNT loading rate applied during the first three operational periods. Effluent DNT concentrations increased to an average of 0.16 mg/L. On one day, the effluent DNT was observed to be 0.6 mg/L, the only result above the plant discharge limit during the entire study. This effluent concentration from the water-dry wastewater pretreatment system would not result in the plant effluent exceeding the NPDES permit levels. The average removal efficiency for DNT was >99.88%. Effluent ethanol concentrations were below detection limits and the effluent acetate concentration decreased to an average of 10 mg/L, indicating utilization of essentially all of the usable COD (Table 5-8). The lack of sufficient usable COD resulted in a slight decrease in removal efficiencies. With a 15% COD utilization allowance for cell growth, the mass balance indicates 32% more usable COD can be accounted for than was added to the system. As with the previous period, this can probably be attributed to some adsorption of DNT and/or endogenous respiration.

Table 5-8. Usable COD Balance for Operational Period No. 4

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
6/8/95	321	37	284	2.0	96	219	43	11%	30%	68%	13%	123%
6/9/95	271	17	253	1.7	99	118	38	6%	37%	43%	14%	100%
6/12/95	184	0	184	1.1	101	118	28	0%	55%	64%	15%	134%
6/13/95	179	0	179	1.1	105	185	27	0%	59%	103%	15%	177%
6/15/95	168	0	168	1.0	100	126	25	0%	59%	75%	15%	150%
Average	224	11	213	1.4	100	153	32	5%	45%	68%	14%	132%

5.3.5 *Operational Period #5 (6/20/95 to 6/29/95)*

During the fifth operational period, the forward feed rate to the reactor was kept at 0.8 gpm, (HRT of 3.9 hours). Supplemental ethanol was added at 243 mg/L to ensure sufficient reducing power was being fed to the system. The concentration of DNT in the effluent immediately decreased, eventually to below detection limits. A summary of results for this period is presented as Table 5-9.

Table 5-9. Performance Summary for Operational Period No. 5

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
6/20/95	127.5	<0.1	783	>99.9%	290	bdl	14	27	bdl	16	1003	455	5.1
6/22/95	129.67	<0.1	796	>99.9%	341	bdl	17	36	bdl	43	1117	512	6.0
6/27/95	127.3	<0.1	782	>99.9%	315	bdl	20	17	3	38	1053	449	5.5
6/29/95	75.41	0.13	463	99.8%	211	bdl	10	5	3	19	688	162	3.9
Average	115	0.07	706	>99.9%	289	bdl	15	21	1.5	29.0	965	395	5.1

Influent DNT concentration averaged 115 mg/L yielding an applied DNT loading of 706 g DNT/m^3-d, lower than the fourth period but still ca. forty percent higher than that of the first three operational periods. Effluent DNT concentrations decreased with the availability of sufficient usable COD and were below detection limits for three of the four sampling events during the period. The average removal efficiency for DNT was >99.9%. Effluent ethanol concentrations were below detection limits. The effluent acetate and propionate concentrations averaged 21 and 29 mg/L respectively. Eighty nine percent of the usable COD was consumed by the bacterial population (Table 5-10). The mass balance was within 12% of closure this period, good agreement for a field system.

Table 5-10. Usable COD Balance for Operational Period No. 5

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
6/20/95	618	53	565	3.8	68	513	85	9%	11%	83%	14%	116%
6/22/95	727	104	624	4.5	69	555	94	14%	9%	76%	13%	113%
6/27/95	681	76	605	4.2	67	501	91	11%	10%	74%	13%	108%
6/29/95	453	34	419	2.8	40	376	63	8%	9%	83%	14%	113%
Average	620	67	553	3.8	61	486	83	11%	10%	78%	13%	112%

5.3.6 *Operational Period #6 (7/5/95 to 7/14/95)*

During the sixth operational period, the forward feed rate to the reactor was maintained at 0.8 gpm, (HRT of 3.9 hours) and supplemental ethanol rate was maintained at about 223 mg/L. Due to the unavailability of water dry wastewater with a high concentration of DNT, a water dry with a DNT concentration of 62 mg/L was used. A summary of results for this period is presented as Table 5-11.

Table 5-11. Performance Summary for Operational Period No. 6

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
7/5/95	61.1	<0.1	375	>99.8%	302	bdl	7	9	bdl	56	847	401	5.1
7/7/95	66.34	<0.1	407	>99.8%	278	bdl	4	10	bdl	32	797	316	4.6
7/8/95	55.87	<0.1	343	>99.8%	237	bdl	7	11	4	34	710	337	4.1
7/9/95	62.3	<0.1	383	>99.8%	281	bdl	4	8	bdl	29	805	324	4.6
7/10/95	62.25	<0.1	382	>99.8%	291	bdl	3	7	bdl	36	825	324	4.8
7/11/95	61.27	<0.1	376	>99.8%	291	bdl	8	8	3	26	825	318	4.7
7/12/95	57.68	<0.1	354	>99.8%	263	bdl	8	12	4	24	756	356	4.3
7/13/95	57.68	<0.1	354	>99.8%	272	bdl	8	12	4	14	776	356	4.3
7/14/95	62.26	<0.1	382	>99.8%	317	bdl	6	8	bdl	9	871	304	4.9
Average	62	<0.1	373	>99.8%	281	bdl	6	10	1.9	28.8	752	337	4.6

With influent DNT concentration averaging only 62 mg/L, the applied DNT loading decreased to 373 g DNT/m^3-d, 26% lower than for first three operational periods. Effluent DNT concentrations were below detection limits throughout the period. Effluent ethanol concentrations were below detection limits and effluent acetate concentration averaged only 10 mg/L. Ninety one percent of the usable COD was consumed by the bacterial population (Table 5-12). The usable COD mass balance indicates excellent closure.

Table 5-12. Usable COD Balance for Operational Period No. 6

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
7/5/95	636	94	541	3.9	32	334	81	15%	5%	53%	13%	85%
7/7/95	583	59	524	3.6	35	399	79	10%	6%	68%	13%	98%
7/8/95	506	63	443	3.1	30	446	66	12%	6%	88%	13%	120%
7/9/95	590	52	537	3.6	33	498	81	9%	6%	85%	14%	113%
7/10/95	610	62	548	3.7	33	511	82	10%	5%	84%	13%	113%
7/11/95	619	48	571	3.8	32	299	86	8%	5%	48%	14%	75%
7/12/95	561	49	512	3.4	31	394	77	9%	5%	70%	14%	98%
7/13/95	581	34	547	3.6	31	494	82	6%	5%	85%	14%	110%
7/14/95	665	22	643	4.1	33	474	96	3%	5%	71%	14%	94%
Average	595	54	541	3.7	32	428	81	9%	5%	72%	14%	100%

5.3.7 Operational Period #7 (7/19/95 to 7/21/95)

During the seventh operational period, the forward feed rate to the reactor was increased to 1.2 gpm, yielding an empty bed HRT of 2.6 hours. The supplemental ethanol rate was decreased to 14 mg/L to provide a total influent ethanol concentration of 339 mg/L. The DNT level of the available water dry wastewater was 85 mg/L. A summary of results for this period is presented as Table 5-13.

Table 5-13. Performance Summary for Operational Period No. 7

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
7/19/95	76.74	0.03	707	99.96%	271	bdl	92	37	5	13	854	298	6.6
7/20/95	85.53	<0.1	788	>99.9%	349	bdl	117	73	4	36	1041	364	8.6
7/21/95	92.64	<0.1	853	>99.9%	397	bdl	119	54	5	37	1158	362	9.3
Average	85	<0.1	783	>99.9%	339	bdl	109	55	4.7	28.7	1018	341	8.1

With the increase in forward feed rate, the applied DNT loading increased to 783 g DNT/m^3-d. Effluent DNT concentrations averaged 0.01 mg/L for the period. Effluent ethanol concentration was below detection limits while effluent acetate concentration increased to an average of 55 mg/L. Eighty eight percent of the usable COD was consumed (Table 5-14). The mass balance indicates good closure.

Table 5-14. Usable COD Balance for Operational Period No. 7

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
7/19/95	671	60	611	6.2	41	573	92	9%	6%	85%	14%	114%
7/20/95	858	133	725	7.9	45	616	109	16%	5%	72%	13%	105%
7/21/95	963	114	849	8.9	49	601	127	12%	5%	62%	13%	93%
Average	831	102	728	7.7	45	597	109	12%	5%	72%	13%	103%

5.3.8 *Operational Period #8 (7/24/95 to 7/26/95)*

During the eighth operational period, the forward feed rate to the reactor was further increased to 2.0 gpm, yielding an empty bed HRT of 1.6 hours. The supplemental ethanol rate was increased to 188 mg/L to ensure availability of sufficient usable COD. The DNT level of the available wastewater averaged 90 mg/L, ca. the same as in the previous period. A summary of results for this period is presented as Table 5-15.

Table 5-15. Performance Summary for Operational Period No. 8

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
7/24/95	92.36	<0.1	1418	>99.9%	347	4	118	323	bdl	65	1038	789	18.7
7/25/95	89.02	<0.1	1367	>99.9%	648	58	119	429	4	4	1674	811	28.7
7/26/95	89.49	<0.1	1374	>99.9%	619	2	125	397	bdl	6	1612	670	27.2
Average	90	<0.1	1386	>99.9%	538	21	121	383	1.3	25.0	1441	757	24.9

With the increase in forward feed rate, the applied DNT loading increased to 1386 g DNT/m^3-d, the highest DNT loading rate examined. Also, the applied usable COD loading increased to 19.3 Kg/m^3-d, over twice the next highest loading rate, and the usable COD consumption (removal) rate was 11.6 Kg/m^3-d, almost twice the previous high. (Figure 5-2) Effluent DNT concentrations remained below detection limits for the period. The effluent contained measurable ethanol concentrations and effluent acetate concentration averaged 383 mg/L, indicating that the HRT was lower than that required by the existing biomass for complete utilization of the available primary substrate. A longer acclimation period at this condition may have resulted in an increase in the total bacterial population. As shown in Table 5-16, 74% of the usable COD can be accounted for. This is slightly lower than the total seen during the initial acclimation period. During this short period, it is likely that much of the remaining COD consumption was utilized for bacterial growth.

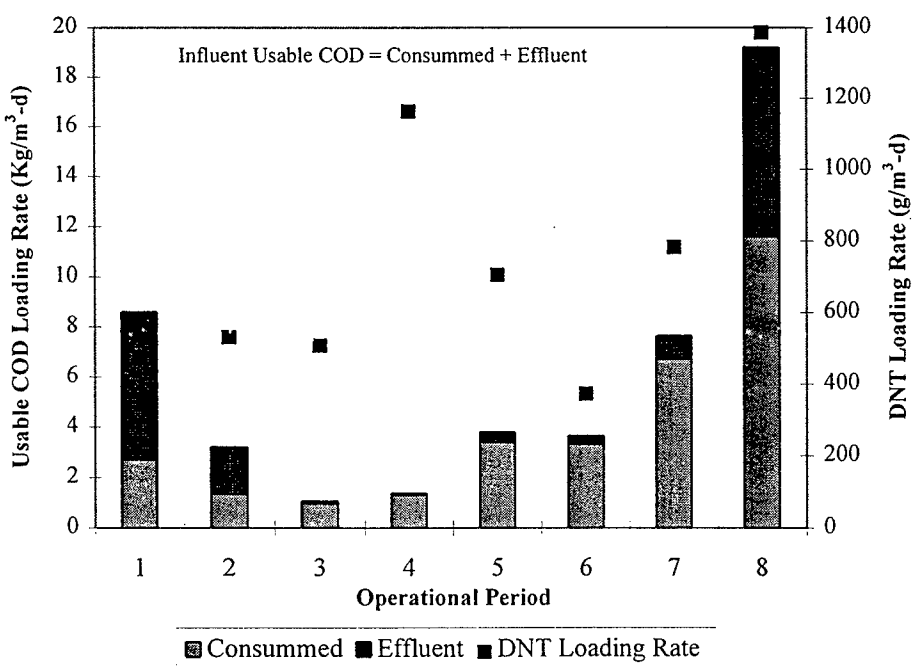

Figure 5-2. Usable COD and DNT Loading Rates

Table 5-16. Usable COD Balance for Operational Period No. 8

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
7/24/95	849	455	394	13.0	49	245	59	54%	6%	29%	7%	95%
7/25/95	1482	590	892	22.8	47	252	134	40%	3%	17%	9%	69%
7/26/95	1423	442	981	21.8	47	320	147	31%	3%	23%	10%	67%
Average	1251	496	756	19.2	48	272	113	40%	4%	22%	9%	74%

6 Performance Summary

The anaerobic GAC-FBR system effectively removed DNT from propellant water dry wastewater over a range of conditions and influent concentrations. DNT was essentially stoichiometrically transformed to DAT. A performance summary for eight operational periods, during which performance was intensively monitored, is shown in Table 6-1. Effluent DNT concentrations at this high strength source were reduced to below the plant effluent discharge limits for the RAAP site for all of the periods except one. During this one period it was found that there was insufficient usable COD available to maintain sufficient reducing power for transformation of all the DNT in the influent. The maximum allowable loading rate for DNT was not determined. Despite several serial increases in the applied loading rates, the limited volume of water dry wastewater available made it impossible to achieve a sufficiently high DNT loading rate to cause less than 99.8% removal.

Table 6-1. Performance Summary for Intensively Monitored Operational Periods

	Dinitrotoluene				Ethanol		Acetate		Propionate		COD		
Date	Influent (mg/L)	Effluent (mg/L)	DNT LR (g/m^3-d)	% Removal	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	OLR (Kg/m^3-d)
1/31/95-2/16/95	155	0.04	476	99.98%	1320	526	52	757	bdl	4.6	3239	1840	10.0
4/17/95-4/28/95	173	<0.05	532	100.00%	491	16	23	529	bdl	1.2	1641	848	5.1
5/30/95-6/7/95	166	<0.06	508	99.99%	150	bdl	30	26	0.3	bdl	760	389	.1.6
6/8/95-6/15/95	189	0.16	1163	99.88%	91	bdl	32	10	bdl	bdl	688	398	2.3
6/20/95-6/30/95	115	0.07	706	99.96%	289	bdl	15	21	1.5	29.0	965	395	5.1
7/5/95-7/14/95	62	<0.10	373	100.00%	281	bdl	6	10	1.9	28.8	752	337	4.6
7/19/95-7/21/95	85	<0.10	783	99.99%	339	bdl	109	55	4.7	28.7	1018	341	8.1
7/24/95-7/26/95	90	<0.10	1386	100.00%	538	21	121	383	1.3	25.0	1441	757	24.9

6.1 *Usable COD:DNT Requirements*

The usable COD:DNT ratio for each operational period was compared with the resulting removal efficiencies to determine the minimum COD requirements and under what situations supplemental ethanol would be required. As shown in Figure 6-1, removal efficiencies of at least 99.97% (and effluent concentrations well within regulatory requirements) were achieved during the first three periods, as the usable COD:DNT ratio was reduced from 18.1 to 6.0 to 2.1. When the ratio was reduced further to 1.2 during the fourth period, removal efficiency decreased to just below 99.9%, and the single effluent concentration exceeding the plant effluent NPDES limit during the entire demonstration period was observed. Increasing the ratio to 5.4 for the fifth period resulted in DNT removal efficiency rebounding. COD:DNT ratios of 9.6, 9.8, and 13.9, respectively, for the final three periods yielded removal efficiencies of at least 99.98%. To ensure acceptable performance, a minimum usable COD:DNT ratio of 3 was assumed for the economic analysis.

6.2 *Usable COD Balance*

The utilization of usable COD for DNT reduction, methane production, and cell growth is summarized in Table 6-2 and depicted graphically in Figure 6-2. A mass balance of usable COD consumed vs. the above utilization "sinks" for COD gave reasonable to excellent closure for all periods. The first and last periods, however, slightly under account for the influent usable COD. The first period was the initial acclimation and biomass growth period and the last period was a brief period following a significant increase in applied OLR. As explained earlier, it is reasonable to expect that a higher driving force for biomass accumulation would have caused a higher fraction of available energy to be directed to cell synthesis during these periods.

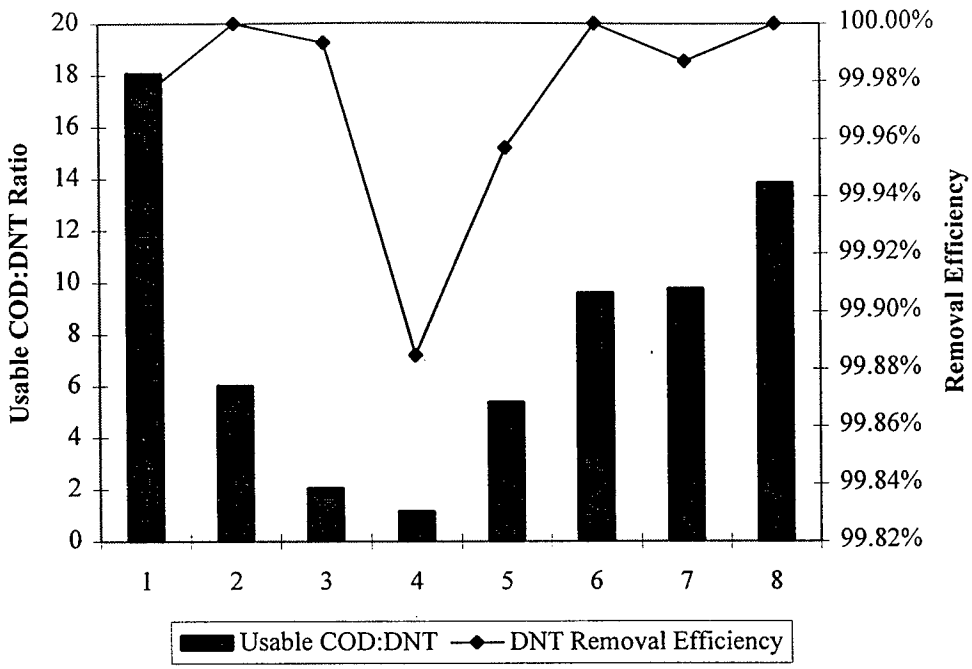

Figure 6-1. Usable COD:DNT Ratio and Removal Efficiency

Table 6-2. COD Balance for Intensively Monitored Operational Periods

Date	Influent (mg/L)	Effluent (mg/L)	Consumed (mg/L)	OLR (Kg/m^3-d)	DNT Reduction (mg/L)	CH_4 Production (mg/L)	Cell Production (mg/L)	Effluent Usable COD (%)	DNT Reduction Usable COD (%)	CH_4 Production Usable COD (%)	Cell Production Usable COD (%)	Total Accounted for Usable COD (%)
1/31/95-2/16/95	2802	1919	882	8.6	82	298	132	69%	3%	11%	5%	87%
4/17/95-4/28/95	1046	607	439	3.2	92	270	66	58%	9%	26%	6%	99%
5/30/95-6/7/95	344	28	316	1.1	88	303	47	8%	25%	88%	14%	135%
6/8/95-6/15/95	224	11	213	1.4	100	153	32	5%	45%	68%	14%	132%
6/20/95-6/30/95	620	67	553	3.8	61	486	83	11%	10%	78%	13%	112%
7/5/95-7/14/95	595	54	541	3.7	32	428	81	9%	5%	72%	14%	100%
7/19/95-7/21/95	831	102	728	7.7	45	597	109	12%	5%	72%	13%	103%
7/24/95-7/26/95	1251	496	756	19.2	48	272	113	40%	4%	22%	9%	74%

6.3 *DNT and Degradation Products*

Influent DNT and effluent DAT concentrations, on a molar basis, for the entire demonstration period are shown in Figure 6-3. Stoichiometrically, complete reduction of one mole of DNT forms one mole of DAT. Initially, the DAT formed was adsorbed onto the GAC carrier. As the DAT level on the GAC increased, DAT began to partition between the GAC and the effluent water on an equilibrium basis. This trend is evident in Figure 6-3. Effluent DAT levels reached equivalence with influent DNT levels on June 19. From then to the end of the demonstration, the DNT level in the influent decreased several times; effluent DAT concentrations followed a similar trend. Effluent DAT concentrations were actually slightly higher than could be accounted for due to reduction of the inlet DNT concentration. This was caused by desorption of previously sorbed DAT.

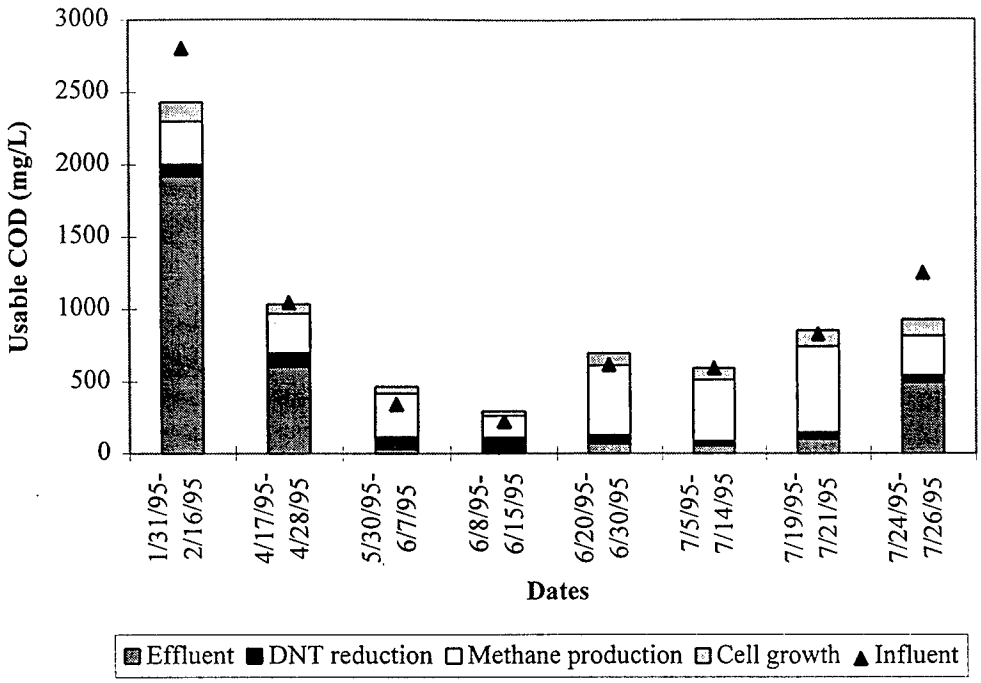

Figure 6-2. Usable COD Mass Balance

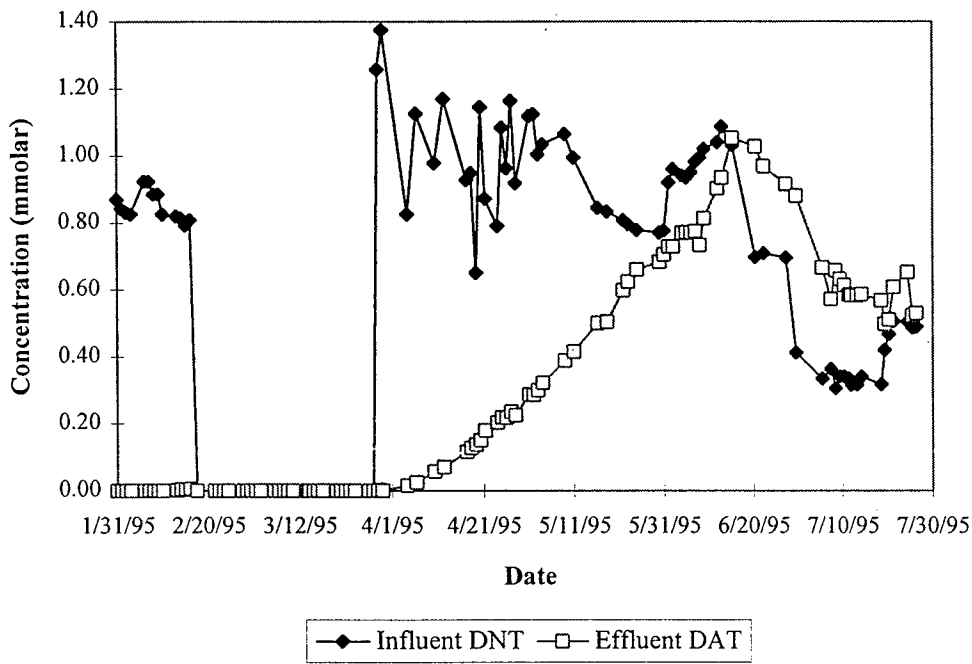

Figure 6-3. Influent DNT versus Effluent DAT

6.4 Analysis of Adsorbed DNT and Degradation Products on GAC

GAC from the reactor was sampled several times during the course of the project and analyzed for adsorbed DNT and DAT. No DNT was recovered from any of the samples. This confirmed that the complete transformation of DNT to DAT and other species occurred. Complete transformation of DNT was further confirmed by the absence of the partially reduced product,

aminonitrotoluene, in any of the samples. DAT, by contrast, was observed for all GAC samples taken from 4/17/95 on. The time course of DAT levels recovered from the GAC is shown in Figure 6-4.

The theoretical mass of DAT that would be expected to be retained on the GAC was calculated based on the reactor throughput and measured influent and effluent concentrations of DNT and DAT, assuming complete reduction of DNT to DAT. This calculated value is compared with the measured values in Figure 6-5. The measured values are consistently lower than the calculated values but follow a similar trend.

There are several reasons why the measured values were lower than the calculated values. Recoveries of spiked samples from the adsorbent in the cold trap averaged 90%, indicating that the measured concentrations are on the order of 10% low. Further, it is quite possible that some DAT is irreversibly sorbed onto the GAC and not recoverable via the thermal desorption analysis method used herein. DAT recoveries from spiked samples trapped on GAC instead of on the adsorbent resin indicated some irreversible adsorption. In addition, some condensation products were formed during the transformation of DNT. Presence of these products was confirmed by GC-MS analysis. Finally, some of the DAT may have polymerized, and would thus not have been recovered as DAT in the analysis.

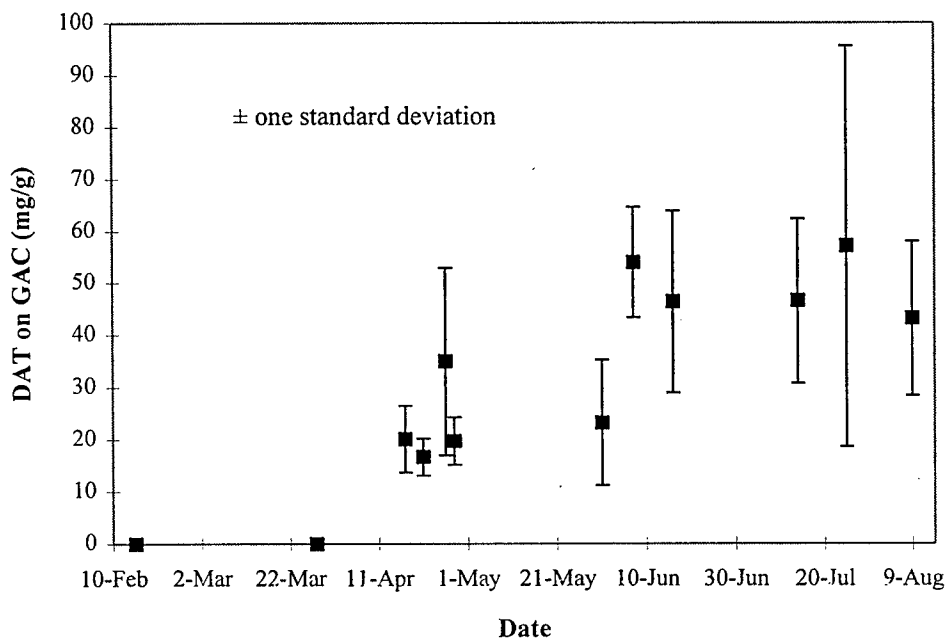

Figure 6-4. DAT on GAC Analysis

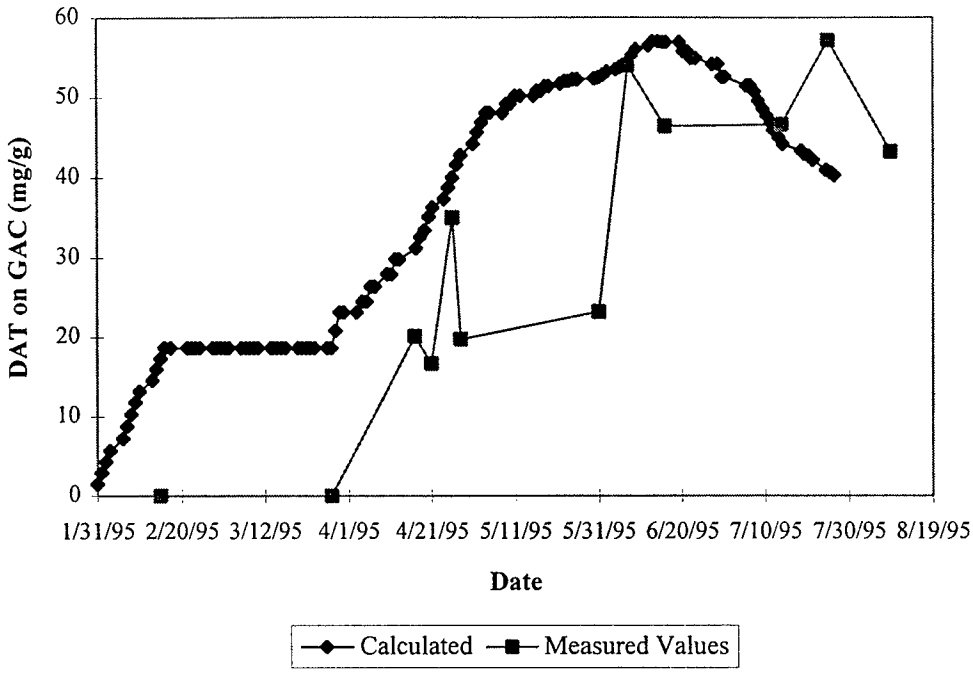

Figure 6-5. Calculated versus Measured DAT on GAC

7 Decommissioning of the GAC-FBR

On August 8-10, 1995, the GAC-FBR system was decommissioned and prepared for movement to another site. The GAC was siphoned into five gallon pails for shipment to MBI/EFX. Sodium hydroxide was then added to the system and allowed to circulate overnight to clean the system. The recirculating water was then neutralized by acid addition, and drained to the sewer line feeding RAAP's wastewater treatment plant. The reactor was then rinsed with clean water.

Once the system was drained, the reactor was partially disassembled and prepared for shipment. This included removal of the WTGM, gas sample conditioner, and IRGA, and disassembly of the separator, GAC return pump, and effluent and recycle downcomers. The pH and DO probes were removed and packaged to protect the sensors. The influent and effluent lines were disconnected at the flanges. Other piping was loosened or removed to avoid breakage during shipping. The nutrient and pH control tanks were emptied and flushed.

The clean and empty reactor was then left in place for final disassembly by AlliantTechSystems's riggers and shipment to the new site.

8 Design Criteria and Economic Evaluation for a Production Scale GAC-FBR

8.1 Summary of Design Criteria

The design criteria proposed for the RAAP site for treatment of DNT containing water-dry wastewater treatment is based on their current estimated production level of 3.5 to 4.0 million pounds of DNT based propellants per year over the next five years.

RAAP currently has eight active water-dry buildings, and anticipates that these will be adequate for current production levels. Each building can process 40,000 pounds of propellant in an 11 to 14 day cycle, resulting in generation of 8,000 gallons of water-dry wastewater per building per cycle. The design treatment rate of 4 gpm is the maximum generation rate that would result from simultaneous use of all eight buildings on an 11 day cycle.

The design concentrations for influent DNT and usable COD (ethanol and acetate) are the average concentrations measured over the period from 3/29/95 to 6/15/95 (Table 8.1). This period had the highest sustained DNT concentrations seen during the course of this demonstration project (Figure 8.1). The DNT treatment rate at the maximum design flow rate and these concentrations is 3.9 Kg DNT/d.

Table 8-1. Design Influent Concentrations (mg/L)

Component	Average	Std. Dev.	Range
DNT	178	27	119-252
Ethanol	193	57	66-257
Acetate	26	5	18-39

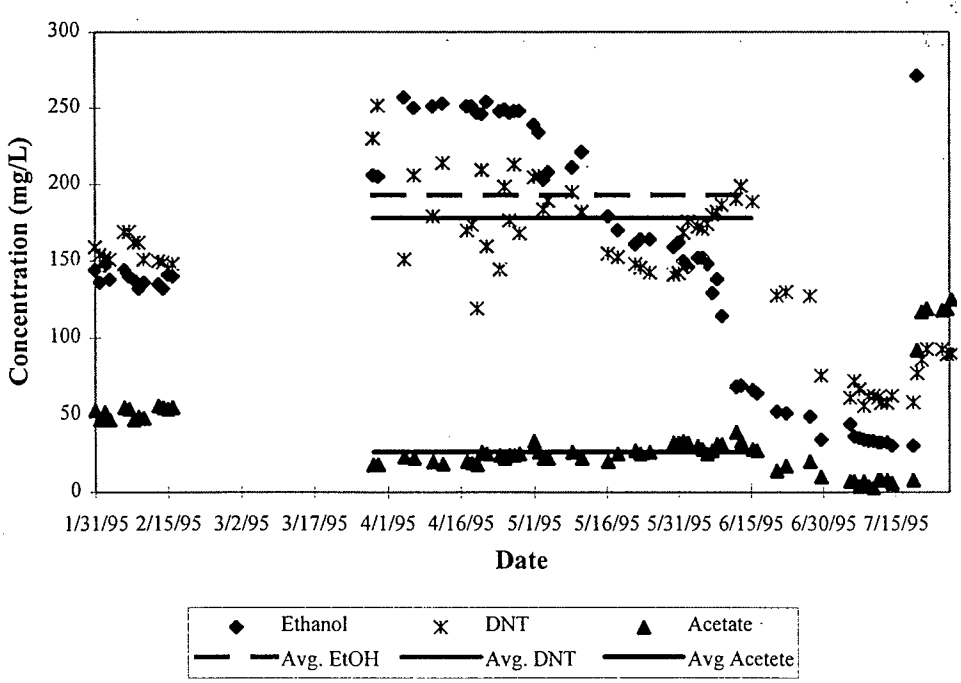

Figure 8-1. Design Influent Concentrations

8.2 GAC-FBR System Specification

As discussed in Section 6, due to the limited amount of water-dry wastewater available during this demonstration, it was not possible to achieve an applied DNT loading rate high enough to define the maximum DNT transformation capacity of the GAC-FBR system. The system specification recommended herein is conservatively based on the maximum loading rate tested. This specific loading rate, achieved during the eighth operational period, was 1.4 Kg DNT/m^3-d.

The GAC-FBR system recommended for installation at RAAP is a Model 190 system. This system is the next standard size up from the Model 30 utilized for this demonstration. It has a 5.2 m^3 working bed volume. At the maximum DNT loading rate successfully demonstrated during this project, the Model 190 has the capacity to treat 7.2 Kg DNT/d. This results in a safety factor (SF) of 1.85. Because the design criteria is such that the anticipated annual production requirements could be met using the currently active water dry buildings for less than half of the available time, the Model 190 has capacity to successfully treat RAAP's DNT containing water-dry wastewater even if production requirements quadrupled.

The system would be set up similarly to the Model 30 used for the demonstration except that the gas measurement and analysis equipment would be omitted. The system would be controlled by a PLC, interfaced with a modem equipped computer and autodialer such that system performance can be remotely accessed. The autodial system would alert on-call personnel of immediate needs for operator attention. This feature reduces operating costs by eliminating the need for frequent on-site monitoring.

8.3 GAC-FBR System Economic Analysis

The capital cost for the anaerobic GAC-FBR as detailed above was estimated at $225,000. This assumes that there is an existing building and pad to house the GAC-FBR system. The total operating and maintenance cost, less labor, is estimated at $8.06 per day or $2,940 per year. A breakout of O&M costs is shown in Table 8-2, and the details for each category are indicated below. Labor requirements consist of periodic operational checks, preparation of supplemental ethanol, pH control, and nutrient solutions, and system sampling. The PLC controller and auto-dialer included with the system reduce labor requirements by monitoring system parameters and alerting on-call personnel to any conditions requiring on-site attention. As the labor costs for the GAC-FBR system should be minimal, and further should be comparable to those for liquid phase GAC adsorption, these costs were omitted from this analysis and from the comparison of the two technologies.

Table 8-2. Estimated Operation and Maintenance Cost for an Envirex Model 190 Anaerobic GAC-FBR Treating RAAP Water-dry Wastewater Containing DNT

Cost Category	Daily Cost	Annual Cost
Electrical power	$4.99	$1821
Supplemental 2T ethanol	$0.36	$132
Supplemental nutrients	$2.35	$859
GAC attrition	$0.36	$130
Total O&M (less labor)	$8.06	$2942

Assuming the COD and DNT concentrations used in this analysis (Table 8-1) represent the long term concentrations at RAAP, maintenance of a usable COD to DNT ratio of 3 in the water-dry wastewater would require 100 mg/L (0.22 gpd) supplemental ethanol. At RAAP's contract price of $1.65/gal for 2-T ethanol, this would cost $0.36/day.

The nutrient requirements were estimated assuming costs of 1.25 times the current bulk price listed in the Chemical Marketing Reporter for sodium phosphate and urea, and twice the current bulk price for the trace minerals required. The total daily nutrient cost was estimated at $2.35.

Electrical power requirements were estimated from known horsepower/current draw for electrical components, estimated usage, and the actual power costs for the January-November time period at RAAP. For the economic analysis, it was assumed that the influent does not require preheating; the in-line influent heater is capable of warming 45°F influent to the design 95°F operating temperature. The total daily power cost was estimated at $4.99.

Loss of GAC from the system (attrition and carryover) was estimated at 5% annually. This is a conservatively high estimate compared to field results. The average daily cost for replacement is $0.36.

8.4 Cost Comparison to Liquid Phase Carbon Adsorption

The costs estimated above for the anaerobic GAC-FBR system were compared to the cost projection for the liquid phase GAC adsorption system currently rented from Envirotrol, Inc. (Sewickley, PA) and in use at RAAP. The predicted maximum loading of 72 pounds used in this analysis was based on the results of the pilot study conducted by Envirotrol at RAAP.

The initial delivery of the rental adsorption unit to RAAP cost $2,300. The initial activated carbon charge (3,600 pounds virgin GAC) cost $3060. System rental cost is $1,875 per month. Changeout service, including removal and treatment of the spent carbon and recharging with virgin carbon, costs $5,710 per event. Based on the design production rate and DNT concentration in the wastewater, 1,186 pounds of DNT would have to be removed annually. That would require 16.5 changeout services at an annual cost of $94,215. The rental also specifies a one-time $2,300 demobilization cost. Power costs for pumping wastewater through the filter were not included. As with the anaerobic GAC-FBR system, labor requirements were also not included.

The annualized cost for each system was computed assuming a 7% annual interest rate and a 20 year useful life. A breakdown of the annualized costs for both systems is shown in Table 8-3. Demobilization costs were not included for either system; they are minor compared to initial or annual O&M costs. The total annualized cost for the GAC-FBR is only 21% of the annualized cost for the liquid phase GAC adsorption system. The total cost for the first three years is plotted in Figure 8-2. The lower O&M cost for the anaerobic GAC-FBR system, $2,942 vs. $116,715 for the liquid phase GAC, results in payback of the capital investment required for the GAC-FBR in less than two years.

Table 8-3. Cost Comparison for Anaerobic GAC-FBR versus Liquid Phase GAC Adsorption

Item	GAC-FBR	Liquid GAC
Amortized capital cost (7%, 20 year)	$21,240	$506
Operation and Maintenance		
Rental, $1,875/mo.		$22,500
Changeout service, $5,710/event		$94,215
Total annual O&M	$2,942	$116,715
Total first year cost		
Total annualized cost	$24,182	$117,221

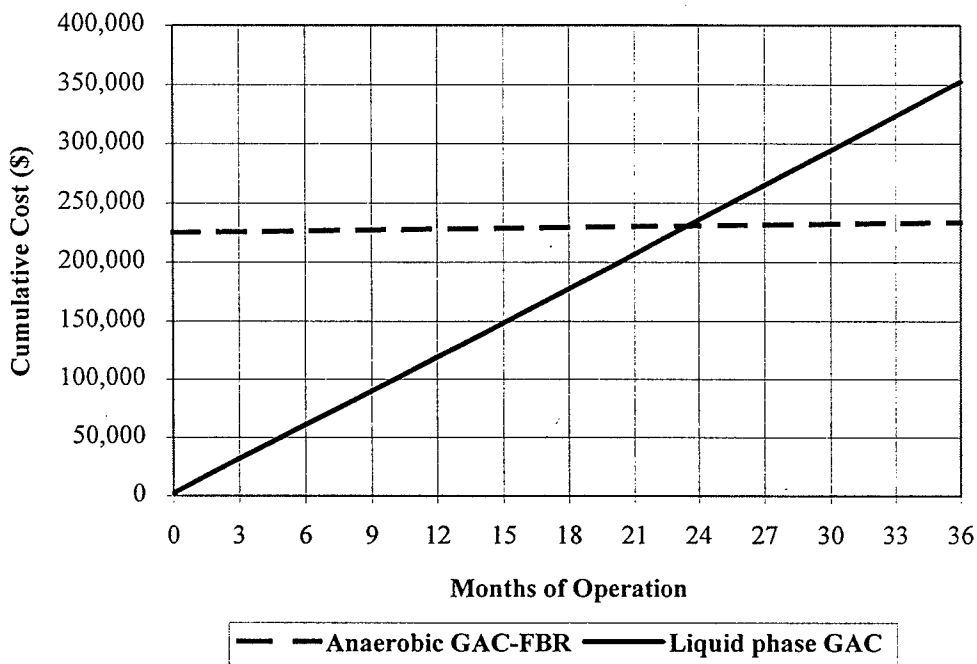

Figure 8-2. Total Cost Comparison for GAC-FBR versus Liquid Carbon Adsorption

APPENDIX A

METHODS AND MATERIALS

APPENDIX A. METHODS AND MATERIALS

A.1 Routine Analytical Methods

All routine analyses were performed by the GOCO on site, AlliantTechSystems. The analytical methods used by AlliantTechSystems for the analyses of untreated and treated wastewater samples in this demonstration were taken from "Standard Methods for the Examination of Water and Wastewater, 18th Edition," the U.S. EPA's "Test Methods for Evaluating Solid Waste" (EPA/SW-846), and AlliantTechSystems Technical Analytical Operating Procedures. The specific analytical methods for the critical parameters, DNT and DAT, are shown in Table A-1. Analytical methods for non-critical parameters are shown in Table A-2. Quantitation of DNT, the key analytical parameter, and DAT were conducted as described in AlliantTechSystems' Chemical Laboratories Procedure Manual: "Determination of 2,4-Dinitrotoluene, 2,4-Diaminotoluene and 2,4,6-Trinitrotoluene in Wastewaters by HPLC" (Procedure No. L-TA-7, issued 05/93) when the DNT and DAT concentrations were excess of 100 ug/l. When the DNT or DAT concentration was less than 100 ug/l, a Kuderna-Danish (K-D) distillation was performed to concentrate the sample prior to analysis by AlliantTechSystems' Procedure No. L-TA-7. The detection level by a K-D distillation was 10 ug/l.

Quantitation of alcohol and ether was conducted as described in AlliantTechSystems' Chemical Laboratories Procedure Manual, Procedure No. L-TA-43. Volatile fatty acids were measured by the method developed by the University of Cincinnati (UC) and modified by AlliantTechSystems.

Except for analyses of DNT and transformation products on GAC conducted by EFX, all analyses were conducted by AlliantTechSystems' Technical Analytical Group located on-site at the Radford Army Ammunition Plant. Samples submitted for analysis were submitted in accordance with AlliantTechSystems' "Protocol and Regulations for Sample Submission to the Technical Analytical Group"

A.2 Quality Control Checks

Laboratory control standards (LCS) were routinely used in analyses to establish that an instrument or procedure was operating within control limits before analysis of samples began. The LCS were prepared by adding known quantities of stock materials to deionized water or by purchasing pre-made standards. The results had to be within control limits before sample analysis was begun. The LCS were used for all analyses during this test program. LCS analyses were performed daily before sample analysis. A calibration check or an LCS sample was run after every 10 to 15 samples to verify that the calibration was still in control.

The quality control (QC) procedures for DNT and DAT analyses, summarized in Table A-3, were designed specifically for this task. These samples consisted of laboratory control standards, matrix spikes and matrix spike duplicates, and methods of addition.

A.3 AlliantTechSystems Sampling Procedures

Samples were collected at the times and locations specified in Sections 3 and 4 of the Test Plan as modified during the course of the demonstration. A sufficient quantity of sample was collected to ensure that the analyses and all QA/QC procedures could be properly conducted. Table A-4 presents the volumes of samples required for analyses. In addition, Table A-4 presents the required sample containers, preservation methods, and maximum holding times for the samples collected during the demonstration.

Each sample was assigned a unique alpha-numeric sample identification number. This consisted of the AlliantTechSystems' Project No. (ME-127), the technology demonstration (AnBAC), the sample location identifier, and the test run number. Sampling events were documented on the operations logs maintained at the site.

A.4 Sample Packaging

The samples analyzed on-site by AlliantTechSystems were placed in a sample cooler, and hand delivered to the appropriate laboratory.

Samples of GAC for analysis by EFX Systems were placed in 40 ml I-Chem containers and cooled to 4°C. The sample containers were packed with bubble pack, or other protective material, to avoid breakage and in vermiculite to absorb liquids should breakage occur. The sample containers and protective packaging were placed in a sturdy shipping container (e.g., plastic cooler) for shipment via Federal Express overnight delivery service. Federal Express collected packages for delivery daily from Building No. 220 at RAAP.

A.5 DNT and Transformation Products on GAC

Samples of GAC were analyzed for DNT and transformation products by a two stage desorption method using a Perkin Elmer ATD-400 coupled to a Perkin Elmer Autosystem Gas Chromatograph. Weighed GAC samples were placed in a sample tube and heated to transfer all volatile components onto a cold sample trap. The sample trap was then heated rapidly and the released volitiles were carried by inert gas into the gas chromatograph. The ATD/GC system was calibrated using a five level addition of DNT and DAT on glass wool. Multiple desorptions from a single GAC sample confirmed that first pass recoveries averaged 90% of the total adsorbed DNT/DAT.

TABLE A-1. SUMMARY OF ANALYTICAL METHODS FOR CRITICAL PARAMETERS(+)

Parameter	Method	Measurement Units	Minimum Detectable Level	Precision (RPD)	Accuracy (% Recovery)	Completeness
DNT	L-TA-7(*) (HPLC Direct Injection)	mg/l	0.1	25	80 - 120	90
	L-TA-7 (*) (Sample Preparation by K-D Distillation)	mg/l	0.01	25	38 - 120	90
DAT	L-TA-7(*) (HPLC Direct Injection)	mg/l	0.2	25	80 - 120	90
	L-TA-7 (*) (Sample Preparation by K-D Distillation)	mg/l	0.01	25	38 - 120	90

(+) - Internal Quality Control Checks for DNT and DAT are included in Table A-3

(*) - AlliantTechSystems Technical Analytical Procedure

TABLE A-2. SUMMARY OF ANALYTICAL METHODS FOR NON-CRITICAL PARAMETERS

Parameter	Method	Measurement Units	Minimum Detectable Level
Volatile Fatty Acids	(GC) (1)	mg/l	10
Alcohol	L-TA-43 (2) (GC)	mg/l	1
Ether	L-TA-43 (2) (GC)	mg/l	1
COD	Hach kit	mg/l	1
Sulfate	4500-SO4 B (3,4) (ion chromatography)	mg/l	5

(1) - Method developed by the University of Cincinnati and modified by AlliantTechSystems during a previous study

(2) - AlliantTechSystems Technical Analytical Procedure

(3) - Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992

(4) - 4500-SO4 E (Turbidimetric) may be used as an alternative

TABLE A-3. SUMMARY OF INTERNAL QUALITY CONTROLCHECKS FOR CRITICAL PARAMETERS (+)

Parameter	QC Check	Frequency	Acceptance Criteria
DNT	Initial Calibration, 5 point	Initially	Relative Standard Dev. (RSD) < 20%
(HPLC direct injection)	Continuing Calibration, mid-point	Daily	+/- 15% of initial calibration
	Matrix Spike	Weekly	80-120% Recovery(*)
DAT	Matrix Spike Duplicate	Weekly	+/- 25% Relative Percent Diff. (RPD)
(HPLC direct injection)			
	Initial Calibration, 5 point	Initially	Relative Standard Dev. (RSD) < 20%
	Continuing Calibration, mid-point	Daily	+/- 15% of initial calibration
	Matrix Spike	Weekly	80-120% Recovery(*)
	Matrix Spike Duplicate	Weekly	+/- 25% Relative Percent Diff. (RPD)

(+) - Analytical Methods for DNT and DAT are included in Table A-1

(*) - For DNT/DAT concentrations > 1 mg/l

TABLE A-4. SAMPLE VOLUME, CONTAINERS, HOLDING TIMES, AND PRESERVATION

Sample	Volume Required	Sample Container	Maximum Holding Time	Preservation
DNT and DAT (Direct Injection)	40 ml	Amber glass vial, Teflon lid liner	3 days	Cool, 4°C
DNT and DAT (K-D Distillation)	1 L each	Amber glass, Teflon lid liner	3 days	Cool, 4°C
Volatile fatty acids	40 ml	VOA vial	3 days	H_3PO_4, pH<2
Alcohols and Ethers	40 ml	VOA vial	3 days	Cool, 4°C H_3PO_4, pH<2
Chemical Oxygen Demand	1 gallon	Plastic jug	5 days	Cool, 4°C
Sulfate	250 ml	Plastic	3 days	HNO_3, pH<2

APPENDIX B

ANALYTICAL RESULTS

Appendix B. Analytical Results

Date	Ethanol		Ether		Acetate		Propionate		COD		DNT		DAT	
	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff
1/30/95		583		6.5		850		10.3		2038		0.103		
1/31/95	144	584	64	6.4	53	786	0	7.8	763	2100	159	0.111		
2/1/95	136	567	61	8.3	47	817	0	8	763	2138	154	0.11		
2/2/95	147	445	63	9.9	52	768	0	6.7	788	1888	152	0.117		
2/3/95	138	464	71	15	47	922	0	8.2	625	1950	151	0.113		
2/6/95	144	152	63	14	55	1031	0	14.9	675	1325	169	0		
2/7/95	140	263	69	16	54	852	0	7.2	650	1375	169	0		
2/8/95	138	0	60	17	47	451	0	31	725	625	162	0	0.26	0
2/9/95	132	143	57	19	49	670	0	2.1	750	1025	162	0	0.03	0
2/10/95	136	675	68	24	48	678	0	0	728	1700	151	0	0.65	0
2/13/95	135	672	61	29	56	652	0	0	728	1800	150	0	0.81	0.21
2/14/95	132	690	63	37	55	648	0	0	725	2125	149	0	0.89	0.41
2/15/95	141	739	67	31	54	690	0	0	670	2200	145	0	1.01	0.49
2/16/95	140	919	61	38	55	574	0	0	655	2450	148	0.01	0.99	0.74
2/17/95														
2/21/95														
2/22/95														
2/23/95									3.1	483				
2/24/95														
2/27/95														
2/28/95														
3/1/95														
3/2/95	49	21.6	21.8	22.1	395	404	0	0	527	476				
3/3/95														
3/6/95														
3/7/95	635	624	21.2	21.2	198	202	0	0	1455	1480				
3/8/95														
3/9/95	601	597	19.9	20.2	316	325	0	0	1585	1590				
3/10/95														
3/13/95														
3/14/95	596	602	18	20	350	369	0	0	1632	1622				
3/15/95														
3/16/95	654	686	21	18	387	393	0	0	1806	1824				
3/17/95														
3/20/95														
3/21/95	432	440	20.1	19.6	319	325	0	0	1166	1164				

Appendix B. Analytical Results

Date	Ethanol		Ether		Acetate		Propionate		COD		DNT		DAT	
	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff
3/22/95														
3/23/95	587	577	21.4	23.3	374	387	0	0	1494	1470				
3/24/95														
3/27/95														
3/28/95	r flow at 0.4 gpm on 3/28/95													
3/29/95	206	194	95	14	17.6	534	0	0	928	920	230	0	2.8	0.22
3/30/95	205	132	83	17	17.9	497	0	0	994	786	251.5	0	0	0
3/31/95														
4/3/95														
4/4/95	257	0	114	35	23	577	0	8.3	1100	745	151	0	0	1.89
4/5/95														
4/6/95	250	0	118	44	22	575	0	6.1	1235	745	206	0	0	3.03
4/7/95														
4/10/95	251	0	115	73	19.7	327	0	4	1115	485	179	0	0.372	6.995
4/11/95														
4/12/95	253	26	119	85	18.4	793	0	0	1142	949	214	0	0	8.589
4/13/95														
4/17/95	251	0	126	113	20	488	0	0	1078	707	169.9	0	0.342	14.198
4/18/95	251	0	126	115	19	304	0	0	1126	557	173.7	0	0.306	15.598
4/19/95	247	0	109	112	18	584	0	2	1120	823	119	0	0.283	16.958
4/20/95	246	15	124	114	26	676	0	0	1125	911	209.4	0	0	18.435
4/21/95	254	0	126	122	25	557	0	6.3	1114	842	159.5	0	0.326	22.06
4/24/95	248	0	119	124	24	259	0	2	1068	576	144.58	0	0.504	25.04
4/25/95	249	20	116	130	22	567	0	0	1089	962	198.3	0	0.5	26.89
4/26/95	247	45	117	124	24	624	0	0	1039	1023	176.3	0	0	26.71
4/27/95	248	47	121	132	24	620	0	0	1090	1047	213	0	0.453	28.93
4/28/95	248	36	121	131	25	611	0	2	1042	1028	168.01	0	0.54	27.7
5/1/95	239	0	116	132	33	563	0	2	1094	919	204.65	0	3.3	35.31
5/2/95	234	0	111	134	26	618	0	3	1027	979	205.68	0	1.11	35.13
5/3/95	203	0	74	103	22	525	0	3	953	927	183.7	0	1.86	36.88
5/4/95	208	0	77	102	22	563	0	2	971	921	189.27	0	0.76	39.56
5/5/95														
5/8/95														
5/9/95	211	0	74	91	26	206	0	4	1034	580	194.8	0	0	47.76
5/10/95														
5/11/95	221	0	78	92	22	175	0	4	1025	545	181.92	0	0.383	51.1

Appendix B. Analytical Results

Date	Ethanol		Ether		Acetate		Propionate		COD		DNT		DAT	
	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff
5/12/95														
5/15/95														
5/16/95	179	0	58	87	20	107	0	0	848	499	154.6	0	0.732	61.55
5/17/95														
5/18/95	170	0	67	82	25	117	0	3	822	517	152.38	0.157	0.376	62.06
5/19/95														
5/22/95	161	0	63	74	27	81	0	3	822	456	147.71	0	0.515	73.61
5/23/95	164	0	62	73	25	74	0	3	813	427	145.5	0	0.647	76.8
5/24/95														
5/25/95	164	0	64	76	26	66	0	0	823	417	142.41	0	0.474	81.156
5/26/95														
5/30/95	159	0	56	65	32	41	2	0	805	379	141	0	0	83.98
5/31/95	162	0	59	67	32	37	0	0	806	418	142	0	0	86.638
6/1/95	150	0	58	63	33	40	0	0	803	414	168.46	0	0	89.56
6/2/95	146	0	61	65	32	31	0	0	794	380	175.7	0	0	89.58
6/4/95	152	0	60	64	30	21	0	0	774	367	172.2	0	0	94.65
6/5/95	152	0	61	67	28	18	0	0	768	394	171	0	0	94.84
6/6/95	148	0	58	61	25	14	0	0	788	369	174	0	0	94.76
6/7/95	129	0	60	60	27	7	0	0	770	394	179.8	0.097	0	95.2
6/7/95												0		92.48
6/8/95	138	0	65	66	31	34	0	0	786	396	182	0.064	0	90.2
6/8/95												0		97.12
6/9/95	114	0	64	65	31	16	0	0	744	385	186.6	0.11	0.534	99.98
6/9/95												0		101.96
6/12/95	68	0	62	66	39	0	0	0	686	384	190.36	0.198	0	110.97
6/13/95	69	0	62	66	33	0	0	0	678	415	198.89	0.119	0.549	115.01
6/14/95														
6/15/95	66	0	63	66	28	0	0	0	629	410	188.64	0.6	0	129.5
6/16/95	64	0	65	66	27	0	0	0	669	428				
6/19/95														
6/20/95	52	0	69	63	14	27	0	16	509	455	127.5	0	0	126.42
6/21/95														
6/22/95	51	0	69	63	17	36	0	43	530	512	129.67	0	0	119.17
6/23/95														
6/27/95	49	0	64	63	20	17	3	38	503	449	127.3	0	0	112.58
6/28/95														

Appendix B. Analytical Results

Date	Ethanol		Ether		Acetate		Propionate		COD		DNT		DAT	
	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff	Anal Inf	Anal Eff
6/29/95	34	0	43	58	10	5	3	19	408	162	75.41	0.13	0	108.35
6/30/95														
7/5/95	44	0	42	42	7	9	0	56	336	401	61.1	0	0	81.88
7/6/95	36	0	43	43	7	10	4	28			71.79		0	
7/7/95	35	0	40	41	4	10	0	32	296	316	66.34	0	0	70.28
7/8/95	34	0	43	43	7	11	4	34	292	337	55.87	0	0	80.82
7/9/95	33	0	43	43	4	8	0	29	295	324	62.3	0	0	77.64
7/10/95	33	0	43	44	3	7	0	36	284	324	62.25	0	0	75.43
7/11/95	32	0	40	42	8	8	3	26	294	318	61.27	0	0	71.92
7/12/95	32	0	38	39	8	12	4	24	299	356	57.68	0	0	71.69
7/13/95	32	0	38	39	8	12	4	14	299	356	57.68	0	0	71.69
7/14/95	30	0	39	40	6	8	0	9	296	304	62.26	0	0	72.07
7/18/95	30	0	37	39	8	9	4	14	282	300	58.11	0	0	69.9
7/19/95	271	0	23	33	92	37	5	13	961	298	76.74	0.03	0	61.21
7/20/95	349	0	17	25	117	73	4	36	1151	364	85.53	0	0	62.84
7/21/95	356	0	17	24	119	54	5	37	1178	362	92.64	0	0	74.74
7/24/95	347	4	15	19	118	323	0	65	1177	789	92.36	0	0	80.24
7/25/95	351	58	16	19	119	429	4	4	1176	811	89.02	0	0	64.37
7/26/95	353	2	15	17	125	397	0	6	1168	670	89.49	0	0	65.13

APPENDIX C

PLC DATA SUMMARY

Evaluation of the Application of the Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) for the Treatment of Dinitrotoluene (DNT) at the Radford Army Ammunition Plant (RAAP)

Addendum to the Final Report

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March 7, 1996

Addendum to Section 8 Design Criteria and Economic Evaluation for a Production Scale GAC-FBR

8A.1 Purpose of the Addendum

At the request of Dr. Stephen Maloney, this addendum is provided to address two issues. The first is to modify the economic analysis, using the criteria from the original report, to address operations during periods when there is no DNT containing water-dry wastewater available, and to include labor costs in the analysis. The second issue is to repeat the economic analysis the design criteria used for sizing and costing alternative treatment systems evaluated in other studies.

8A.2 Summary of Original Design Criteria and GAC-FBR System Specification

The original design criteria proposed was based on an estimated production level of 4.0 million pounds of DNT based propellants per year. The design treatment rate of 4 gpm is the maximum generation rate that would result from simultaneous use of all eight currently active water-dry buildings on a minimum 11 day cycle. The design concentrations for influent DNT and usable COD (ethanol and acetate) were the average concentrations measured over the period from 3/29/95 to 6/15/95. This period had the highest sustained DNT concentrations seen during the course of this demonstration project. The DNT loading rate at the maximum design flow rate and these concentrations is 3.9 Kg DNT/d.

The system specified under these design criteria was a Model 190 system. At the maximum DNT loading rate successfully demonstrated during this demonstration, the Model 190 has the capacity to treat 7.2 Kg DNT/d (1.4 Kg DNT/m^3-d), resulting in a safety factor of 1.85 during maximum production periods. Operation at maximum production would result in meeting the annual propellant schedule in 175 days, leaving 190 days for the reactor to operate in a standby mode.

8A.3 Economic Analysis Using the Original Design Criteria

The capitol cost for the Model 190 anaerobic GAC-FBR was estimated at $225,000. This assumes that there were an existing building and pad to house the GAC-FBR system. The total operating and maintenance (O&M) cost was estimated to be $2925 per year without labor and $8,175 per year including labor (Table 8A-1). The costs for operating periods are as originally estimated. The cost for standby operations between propellant production periods was based on maintaining a 1 Kg usable COD/m^3-d applied organic loading rate (vs. 2.24 Kg COD/m3-d during maximum production operations). The reactor was successfully operated at 1 Kg COD/m^3-d during one phase of the demonstration. Labor costs were estimated assuming that operator attention would be required two hours per day, three days per week (0.15 FTE), using an average burdened salary of $35,000 per year.

Table 8A-1. Estimated Operation and Maintenance Cost for a Model 190 Anaerobic GAC-FBR Treating RAAP Water-dry Wastewater containing DNT

Cost Category	Daily Cost		Annual Cost
	Operational (175 days)	Standby (190 days)	
Electrical Power	$4.99	$4.99	$1822
Supplemental 2T ethanol	$0.58	$1.37	$362
Supplemental nutrients	$2.35	$1.05	$511
GAC attrition	$0.36	$0.36	$130
Total O&M less labor	$8.28	$7.77	$2925
Labor	$14.38	$14.38	$5250
Total O&M	$22.66	$22.15	$8175

The total annual O&M cost less labor is $17 per year less than originally estimated when the effects of standby operations are considered as the increase in ethanol requirements is slightly more than compensated for by the savings in nutrients. With a $0.51 daily cost difference between production and standby periods, the total annual cost is insensitive to fluctuations in production requirements, and the system as specified is capable of treating the wastewater from propellant production levels up to fifteen million pounds annually.

8A.4 Alternate Design Criteria

The economic analysis was repeated using a second set of design criteria to facilitate comparison with other treatment systems (i.e. UV/oxidation and liquid GAC adsorption) evaluated in other studies. The same 4,000,000 annual propellant production schedule was assumed, resulting in the same 4 gpm flow requirement. The influent DNT and ethanol concentrations were specified at 100 and 300 mg/L, respectively, for this analysis.

8A.5 Alternate System Specifications

Two different anaerobic GAC-FBR designs capable of achieving effluent criteria with the alternate design criteria were investigated. These designs were a custom Model 70 system utilizing a 30 inch diameter reactor, and a modified Model 30, utilizing a taller reactor column. Both systems were designed to meet plant effluent NPDES standards in the GAC-FBR effluent stream, at DNT loading rates successfully demonstrated at RAAP (1.4 Kg DNT/m^3-d). As the limited availability of wastewater during the demonstration prevented determination of the maximum achievable loading rate for the GAB-FBR system, it is expected that either of these systems would have some excess capacity. In addition, the ability to meet discharge standards with influent concentrations significantly higher than the alternate design criteria has been demonstrated.

8A.6 Economic Evaluation of the Model 70 GAC-FBR

The custom Model 70 system would be very similar to the Model 30 used in the demonstration at RAAP. This system would be operated at a flow rate of 67.5 gpm. The reactor height would be identical to the Model 30, 4.6 m (15 feet). Most of the ancillary equipment

would be the same as on the Model 30 except some of the flow lines and the media separator would be larger. Capitol cost is estimated at $175,000. The fluidization pump would use a 3.0 hp motor vs. 7.5 hp for the Model 190, reducing power requirements. At the design criteria concentrations, the usable COD:DNT ratio is 6.3:1, well over the required 3:1 ratio, so supplemental ethanol would not be required during operational periods. Supplemental ethanol requirements during standby periods would be reduced from those for the Model 190, due to the smaller bed. Nutrient requirements would be reduced during both operational and standby periods, due to the lower organic loading rates. The O&M costs for this system are shown in Table 8A-2.

Table 8A-2. Estimated Operation and Maintenance Cost for a Custom Model 70 Anaerobic GAC-FBR Treating RAAP Water-dry Wastewater containing DNT

Cost Category	Daily Cost		Annual Cost
	Operational (175 days)	Standby (190 days)	
Electrical Power	$2.25	$2.25	$821
Supplemental 2T ethanol	$0.00	$0.41	$78
Supplemental nutrients	$2.26	$0.20	$433
GAC attrition	$0.11	$0.11	$40
Total O&M less labor	$4.62	$2.97	$1373
Labor	$14.38	$14.38	$5250
Total O&M	$19.00	$17.35	$6623

8A.7 Economic Evaluation of the Modified Model 30

A taller version of the current Model 30 GAC-FBR was also included. This was done because USACERL owns the Model 30 used for this demonstration, and that reactor could potentially be modified for use at RAAP. A Model 70 would be the preferred option if the demonstration reactor system were not available.

The standard Model 30 has a usable bed volume of 0.71 m^3. Under the alternate design criteria specified, a bed volume of 1.56 m^3 would be required. This would require a usable bed height of 7.7 m (25.2 feet) and a total column height of 8.5m (28 feet). Modifications of the demonstration system are estimated to cost approximately $20,000. The most significant modifications required for this conversion include:

- extending the column fourteen feet, with appropriate structural support
- providing a caged ladder and platform for access to the top of the reactor
- providing a transfer line from the top of the reactor to the separator
- providing an effluent line from the separator up to the same height as the top of the reactor and back down to the existing line

The current pumps are adequately sized to handle the higher hydraulic head imposed by the taller column. The power requirements would thus be lower than for the Model 70. The bed volume would be the same as for the Model 70, the ethanol requirements during standby

operation, the nutrient requirements, and the GAC attrition would be the same. The O&M costs for this system are shown in Table 8A-3.

Table 8A-3. Estimated Operation and Maintenance Cost for a Modified (28') Model 30 Anaerobic GAC-FBR Treating RAAP Water-dry Wastewater containing DNT

Cost Category	Daily Cost		Annual Cost
	Operational (175 days)	Standby (190 days)	
Electrical Power	$1.18	$1.18	$431
Supplemental 2T ethanol	$0.00	$0.41	$78
Supplemental nutrients	$2.26	$0.20	$433
GAC attrition	$0.11	$0.11	$40
Total O&M less labor	$3.55	$1.90	$982
Labor	$14.38	$14.38	$5250
Total O&M	$17.93	$16.28	$6232

8A.8 Economic Comparison of the GAC-FBR Options

The three options discussed herein, Models 190, 70, and 30 (Tall), were compared to evaluate their capabilities, limitations, and costs over a range of production rates. The capitol cost used for the Model 30 (Tall) was the $20,000 estimated conversion cost plus $150,000, the actual cost of the demonstration system less an allowance for the gas measurement and analysis equipment that would not be required for routine water-dry wastewater treatment.

A brief summary of the design criteria and system capacities is included in Table 8A-4. The Model 190 has the capacity to treat four times the currently estimated requirements at the higher, original design concentration, or almost seven times requirements at the revised design concentration. The Model 70 and Model 30 (Tall) meet the revised design criteria, and can treat the estimated annual production requirements at the lower concentration criteria in 175 days, and thus could treat just over twice the revised annual requirement if run continuously.

Table 8A-4 Design Criteria and Capacity Summary for GAC-FBR Options for Treating Water-dry Wastewater Containing DNT at RAAP

Design DNT concentration, mg/L	178	100	100	100
GAC-FBR Model	190	190	70	30(Tall)
Bed volume, m^3	5.2	5.2	1.56	1.56
Design flow rate, gpm	4	4	4	4
DNT loading, Kg/d	3.9	2.2	2.2	2.2
DNT treatment capacity, Kg/d	7.3	7.3	2.2	2.2
Specific DNT loading rate, Kg/m^3-d	0.75	0.42	1.40	1.40

The capital and O&M costs for the different options are summarized in Table 8A-5. The capital and O&M costs for the Model 190 are higher than for the smaller reactors. The Model 70 and the modified Model 30 are very close in present value, reflecting the small difference in capital cost. As noted earlier in this addendum, the Model 30 (Tall) is only included because it

would be possible to modify the standard Model 30 purchased by USACERL for this demonstration. The Model 70, with a standard column height, would be the preferred configuration to achieve the revised design capacity.

Table 8A-5 Economic Comparison of GAC-FBR Options for Treating Water-dry Wastewater Containing DNT at RAAP

GAC-FBR System	Model 190			Model 70			Model 30(Tall)		
Capital cost	225,000			175,000			170,000		
Amortized capital cost (7%, 20 year)	21,240			16,520			16,048		
Annual propellant production, lb.	2,000,000	4,000,000	6,000,000	2,000,000	4,000,000	6,000,000	2,000,000	4,000,000	6,000,000
Operation and maintenance costs									
Electrical power	1,822	1,822	1,822	821	821	821	431	431	431
Supplemental 2T ethanol	430	362	292	114	78	42	114	78	42
Supplemental nutrients	498	611	725	254	433	615	254	433	615
GAC attrition	130	130	130	40	40	40	40	40	40
Total O&M less labor	2,880	2,925	2,969	1,229	1,372	1,518	839	982	1,128
Labor	5,250	5,250	5,250	5,250	5,250	5,250	5,250	5,250	5,250
Total O&M	8,130	8,175	8,219	6,479	6,622	6,768	6,089	6,232	6,378
Present Value (7%, 10 year)	282,102	282,418	282,727	220,506	221,510	222,536	212,767	213,771	214,796

SECTION 7 - AEROBIC TREATMENT OF KETONES IN GROUNDWATER

Aerobic Treatment of Ketones in Groundwater

Final Report

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EXECUTIVE SUMMARY

A four-month demonstration, using a small commercial-scale biological Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) system was conducted to determine the potential of biologically treating ketones in groundwater. Due to logistical problems, the demonstration was moved from the U.S. Army Waterways Experiment Station in Vicksburg, MS to the pilot plant at MBI International. The system was operated at range of flow rates and applied organic loading rates during these four months. The key results obtained were:

- Acetone, MEK and MIBK could be consistently reduced in concentration by >99%. Effluent concentrations were well below regulatory limitations and, in general, below the method detection limits.

- The rates of degradation observed from highest to lowest were MIBK > MEK > acetone.

- An 86-fold reduction in applied mass loading of ketones per unit volume per day from typical Organic Loading Rates (OLRs) of 3.2 Kg COD/m^3-d to 0.037 Kg COD/m^3-d, resulted in a 20-fold decrease in net kinetic capacity for degradation of acetone, MEK and MIBK in the aerobic GAC-FBR.

- The remaining biomass population still possessed the capacity to degrade 4.4 (acetone) to 20 (MIBK) times more mass of ketones than was fed at this OLR rate, indicating considerable excess capacity.

- The cost of treatment using the GAC-FBR appears quite reasonable, ranging from $0.27 to $1.33 ($/1000 gallons) for 30 to 350 gpm, and a total COD of 43 mg/L and a groundwater temperature of 10°C.

1. INTRODUCTION

1.1 Description of Biological Fluidized Bed Process

The fluidized bed bioreactor is a high rate, biological fixed-film treatment process in which the water to be treated is passed upwards through a bed of fluidized, fine-grained media, such as sand, granular activated carbon or ion exchange resins. Water is passed through the bed at a velocity sufficient to impart motion or fluidization of the media. This occurs when the drag forces caused by the liquid moving past the individual media particles are equal to the net downward force exerted by gravity (buoyant weight of the media). As the water to be treated is passed upwards through the bed of media, contiguous films of microorganisms grow (biofilms) attached to the media. This microbial population removes the organic pollutants from the water using the contaminants for growth and respiration.

Fluidization of fine grained media allows the entire surface of each individual particle to be colonized by bacteria in the form of a biofilm. Surface areas on the order of 300 m2/m3 of bed are common in fluidized bed reactor systems. This results in accumulation of biomass concentrations of up to 50,000 mg VSS/L of fluidized bed, which is an order of magnitude or greater than the cell mass concentrations obtained in most other biological processes, e.g. activated sludge. Fluidization is key to the ability of this process to concentrate active bacterial mass to high levels on small diameter media (<2 mm) without the clogging experienced with packed beds or trickling filters. This superior ability to concentrate active bacterial mass in the reactor has considerable theoretical and kinetic advantages to the performance of the reactor. By manipulating the volume of media added to a system, the fluidization velocity used, and the height that the bed is allowed to expand due to biological (biofilm) growth, a great deal of control of the average biofilm thickness and mean cell retention time can be achieved, optimizing overall process performance. The conceptual advantages of biological fluidized bed reactor systems over conventional biological processes include:

- Large surface area for biomass attachment;
- High biomass concentrations;
- Ability to control and optimize biofilm thickness;
- Minimal plugging, channeling or gas hold-up; and,
- High mass transfer properties through maximum contact between biomass and substrate.

In the mid-1980s, it was recognized that the technology may have the potential of substantially reducing the cost of treating groundwater contaminated with industrial wastes. Currently, at thousands of contaminated sites in the U.S., interdiction wells are used to contain VOC pollutants in the subsurface; water that is pumped from these wells is usually treated with conventional air stripping processes and the effluent air is passed through a granular activated carbon (GAC) module to control VOC emissions. This conventional

system of treating interdicted water with 10 ppm or less of VOCs can cost $1-3/1000 gallons, due mainly to the expense for GAC replacement/regeneration. This indicated that the opportunity for cost reduction lies in the use of biological treatment to destroy most of the pollutant mass instead of loading it on GAC. Yet it was also recognized that a bioprocess that was designed to replace this type of conventional treatment would have to achieve stringent removal capabilities. These included: 1) the ability to remove xenobiotic pollutants (chemicals foreign to biological organisms) at high efficiencies, 2) mobility, 3) the ability to handle a wide range of concentrations and loadings, and 4) resistance to process upsets due to sudden changes in influent concentration and composition. This pointed to the need for implementing the concept of integrating GAC into the biological fluidized bed reactor as the biomass carrier.

Over the past six years, personnel from EFX Systems, Inc. (EFX), a joint venture company between Ecolotrol, Inc. (Westbury, NY) and MBI International (Lansing, MI), in cooperation with Envirex, Inc., has pursued the application of the GAC-FBR for the cleanup of groundwater contaminated with gasoline, complex wastes and a number of industrial process effluents. Laboratory and field-pilot data in this effort indicated that the GAC-FBR has the capability of removing >99% of the total VOCs from groundwater and process effluents, with high removals of semi-volatile compounds as well. Full-scale systems are now operation at field sites with flow rates as high as 4,000 gpm (5.8 million gallons/day).

1.2 Pilot Scale Study of Ketone Removal in a GAC-FBR System

EFX Systems, as a subcontractor to MBI International, conducted a study of destruction of ketones in a pilot scale GAC-FBR System as part of this contract. The results of this laboratory-pilot study were presented in a report issued on January 30, 1995. A brief summary of the experimental results is presented below.

A two-inch diameter, all glass, GAC-FBR was constructed and operated as a single pass system (no recycle), for testing the aerobic treatment of an 8:1:1 mixture of acetone, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK). The reactor feed was supplemented with nitrogen and phosphorous sources to maintain a ratio of COD:N:P of 100:5:1. The GAC-FBR was inoculated with sludge from the East Lansing Municipal Wastewater Treatment Plant.

The study included three steady-state periods with applied organic loading rates (OLR) of 2.3 Kg COD/m3-d, 0.23 Kg COD/m3-d, and 0.025 Kg COD/m3-d, representing a two order of magnitude range of applied OLRs. The effluent concentrations for each ketone for each period were consistently reduced to below detection limits (12.6 μg/L acetone, 7.6 μg/L MEK, 1.1 μg/L MIBK). The hydraulic residence time for all three steady-state periods was seven minutes. The influent pH was maintained at 7.0 throughout the study.

1.3 Field Scale Demonstration of Ketone Treatment Using the GAC-FBR

The current demonstration consisted of set-up of a field scale (30 gpm) reactor in MBI's pilot plant for treatment of a ketone containing wastewater stream. The reactor was located at MBI because of problems gaining timely access to the original site at the USA Waterways Experiment Station in Vicksburg, MS. A synthetic groundwater, consisting of a mixture of city water (groundwater) and a concentrated solution of acetone, MEK, and MIBK (2:1:1 ratio), was fed to the reactor to achieve three applied organic loading rates, covering a 100-fold range, over the course of the demonstration.

1.4 Need for Treatment of Ketones

Low molecular weight, straight-chain ketones such as acetone, MEK and MIBK are among the 100 largest volume organic chemicals used today. These ketones are widely used as solvents for cellulose ethers and esters, nitrocellulose and various natural and synthetic gums and resins. They are also still used in many vinyl resin lacquers and other coatings and as dewaxing agents in the refining of lubricating oils and in extractive distillations.

Ketones are found in leachates and contaminated groundwaters including many RCRA and CERCLA Sites at levels exceeding standards set by the states. These compounds are not readily treated by physical-chemical process such as adsorption onto GAC or air stripping. Ketones are, however, readily degraded biologically. One question concerning biological processes is whether they can continue to operate at low influent ketone concentrations and provide a high degree of removal. Determining the answer to this question was one of the major goals of this work.

2. MATERIALS AND METHODS

2.1 Model 30 GAC-FBR

The present demonstration was conducted using a standard Envirex Model 30 GAC-FBR on loan from Tyndall Air Force Base. The reactor was constructed of 304 stainless steel with a 20-inch diameter, 14.5 foot tall reactor. The reactor had working bed depth of 11.5 feet, yielding a fluidized bed volume of 0.71 m^3. Influent flow to the base of the reactor was maintained at 30 gpm. This was comprised of approximately 2-3 gpm of city water supplemented with a concentrated solution of mixed ketones plus 27-28 gpm recycled reactor effluent. A constant hydraulic flux of 13.8 gpm/SF was maintained throughout the study. The reactor was equipped with a pH control system that can be set to respond to either influent or effluent pH.

Following use at a chemical plant site, this reactor was shipped to Tyndall AFB and stored outside for over one year before being shipped to EFX. During the time at Tyndall, the GAC-FBR was exposed to a salt water environment and was partially submerged in high water during the hurricane season.

Numerous problems, caused by the extreme weather exposure, were encountered and corrected during set-up and pre-start-up inspection. The major problems and corrective actions taken are detailed below in Table 2-1.

Table 2-1. Major Problems and Corrective Action Taken.

Problem Area	Corrective Action
Nutrient system pump failed	• Pump head rebuilt
Air-Sep would not cycle, leaked	• High pressure cut out switch rebuilt (corroded) • Two "T" connectors replaced (corroded, cracked)
pH control system pump failed	• Pump head rebuilt
Air compressor failed to develop pressure	• Unloader control valve rebuilt (corroded) • Unloader relief valve rebuilt (corroded)
Main block valve, feed block valve would not close	• Pressure release solenoid valve rebuilt (corroded)
Oxygen would not feed	• Solenoid block valve rebuilt (corroded) • Control valve actuator rebuilt (corroded) • Control valve rebuilt (corroded)
Fluidization pump #1 failed	• Pump and motor had to be replaced
Pressure gauges failed	• Replaced gauges for fluidization pump discharge, eductor inlet, control air, and oxygen supply pressure.

In addition to the corrective actions listed in Table 2-1, a self-cleaning effluent DO monitoring system was installed and tied in to the oxygen feed control loop.

2.2 Start-up

The reactor was filled with a 350 pound charge of granular activated carbon (GAC) on February 8, 1996. Approximately 5% of this GAC was precoated with a ketone-degrading microbial consortia obtained from the pilot scale reactor used in the laboratory pilot test described in Section 1.2. The system was placed on complete recycle overnight. The following morning influent flow to the reactor was started (5.9 gpm). The initial fluidized bed height after GAC fines were removed, was 99 inches. More detail on the start-up and acclimation period is provided in Sections 3.2 and 3.5.

2.3 Monitoring and Sample Recording

The status of critical reactor components was monitored and recorded daily. A Daily Monitoring Sheet was filled out during each equipment check. The Daily Monitoring Sheet serves as the official record of the conditions in a reactor on any given day of an experiment. This sheet also serves as the official record of directly measured parameters, preparation of solutions or refilling of chemical reservoirs, changes made in reactor parameter set points, and samples taken for analysis. A copy of the Daily Monitoring Sheet is presented in Appendix A.

A detailed record of samples collected was made on a sample log form. Recorded on the log sheet were sample code, date, person collecting the samples, analyst, and analytical results. Analytical results were transferred to this log by the analyst from a printed report from the laboratory information management system used, Turbochrome. The Sample Log Sheet is the official record of the composition of important reactor streams on any given experimental day. A copy of this form is also presented in Appendix A.

All monitoring and analytical records were transferred from the daily monitoring sheet and sample log forms to an Excel spreadsheet. The spreadsheet was used to make appropriate calculations and summary tables. A working copy of the data is maintained on the MBI computer network drive. Backup copies are maintained on tape.

2.4 Sampling, Storage, Analysis and Calibration

Samples were collected in accordance with the schedule shown in Table 2.2.

Influent and effluent DO samples were drawn from sample ports on the reactor and immediately measured using a YSI DO meter. Bed heights were measured by lowering a weighted sampling device into the reactor to the depth at which GAC was encountered. The sampler was then withdrawn and the distance from the top of the reactor to the sampler was measured using a tape measure. Samples for ketone analyses were withdrawn from sample ports on the reactor skid and analyzed by using headspace FID gas chromatography (HS-FID/GC). DO and ketone profile samples were collected by lowering a calibrated length of tubing, with a weighted screened end section on the submerged end, down to the desired depths within the reactor. Water was siphoned until sample from the appropriate depth was

obtained. Samples for both DO and ketones were collected and analyzed as noted above. Biomass on GAC samples were collected from a range of depths in the reactor by lowering a weighted sampler, fitted with a closed lid, to the desired depth. The lid was then opened allowing the container to fill with biofilm coated GAC from that particular depth. The container was then withdrawn from the reactor. VSS/TSS samples were obtained by slowly collecting about a one gallon sample of the stream to be tested. The samples were then filtered and the VSS/TSS measurements were obtained gravimetrically after drying at 105°C and 550°C, respectively. Details of the sampling, storage, analysis, and calibration procedures used for all pertinent tests are included in Appendix B.

Table 2-2. Monitoring Frequency Schedule.

Parameter/Analysis	Start-up	Acclimation Periods	Campaign Periods
Influent/Effluent DO (mg/L)	daily	daily	daily
Bed Height	daily	daily	daily
Influent/Effluent Individual Ketones (mg/L)	daily	2-3 X/week	daily
DO Profile (mg/L)	1 X/week	1 X/week	2-3 X/week
Ketone Profile (mg/L)	1 X/week	1 X/week	2-3 X/week
Biomass on GAC Profile (mg/g GAC)	1 X/week	1 X/week	2-3 X/week
VSS/TSS (mg/L)	1 X/week	1 X/week	daily

3. RESULTS

3.1 Overview of Performance

Throughout this demonstration, with the exception of the initial start-up, greater than 95% (and generally >99%) removal of ketones was consistently observed. Generally, ketones were removed to below detection limits (26 µg/L acetone, 29 µg/L MEK, 43 µg/L MIBK).

3.2 Start-up and Inoculation

The reactor was inoculated on February 8, 1996 with a small volume of GAC that had an active biofilm of ketone degrading organisms. This inoculum was grown in the pilot scale GAC-FBR using a mixture of acetone, MEK and MIBK as the sole carbon source. A portion of the inoculum was removed from the pilot scale reactor over the course of several weeks and stored at 4°C. The remainder was harvested from the pilot scale GAC-FBR and immediately added to the commercial scale unit. Following addition of the inocula, the reactor was fed a small dose of ketones plus the corresponding supplemental nutrients (N and P) and operated on full recycle overnight.

Forward feed to the reactor was started on February 9, 1996. The feed consisted of water from the City of Lansing water supply. A concentrated ketone solution (maximum 5% total ketone) at a 2:1:1 ratio of acetone, MEK, and MIBK, respectively, was premixed in a covered open head 55 gallon drum. The required flow of this solution (17.0 ml/min) was pumped into the influent stream on the suction side of the pump feeding the reactor system to help ensure good mixing and dissolution of the ketones.

3.3 Acclimation and Bed Growth

The system was monitored daily over the following 40 days to track growth of the biofilm, as measured by the increase in height of the fluidized bed, and for ketone removal efficiency. For contaminants that readily adsorb onto GAC, such as BTEX, PAHs and chlorinated solvents, high initial removal efficiency is typically achieved from start-up, due to adsorption. A sufficient biomass population normally accumulates long before the systems adsorption capacity is exhausted. Therefore, high removal efficiency is continuously achieved. Ketones have very little affinity for GAC. Some breakthrough was observed within one day of operation. Never-the-less, greater than 48% removal of ketones was achieved even on day 5, the lowest removal efficiency achieved.

One experimental difficulty experienced during the first eleven days of the demonstration was that inadequate mixing was used in preparing the concentrated ketone solution. This resulted in formation of a layer of free product, predominantly MIBK and MEK, in the feed drum, and correspondingly lower MIBK and MEK concentrations in the

influent to the reactor. The problem was corrected on February 20, by providing more vigorous agitation when preparing the ketone solution.

The initial height of the inoculated fluidized bed on February 9 was 97 inches. The bed grew to reach the control point of 138 inches on February 28 (Figure 3-1); less than three weeks was required to achieve full biofilm growth at an applied organic loading rate of 2.8 Kg COD/m^3-d, even with the period of low inlet ketone concentrations described above.

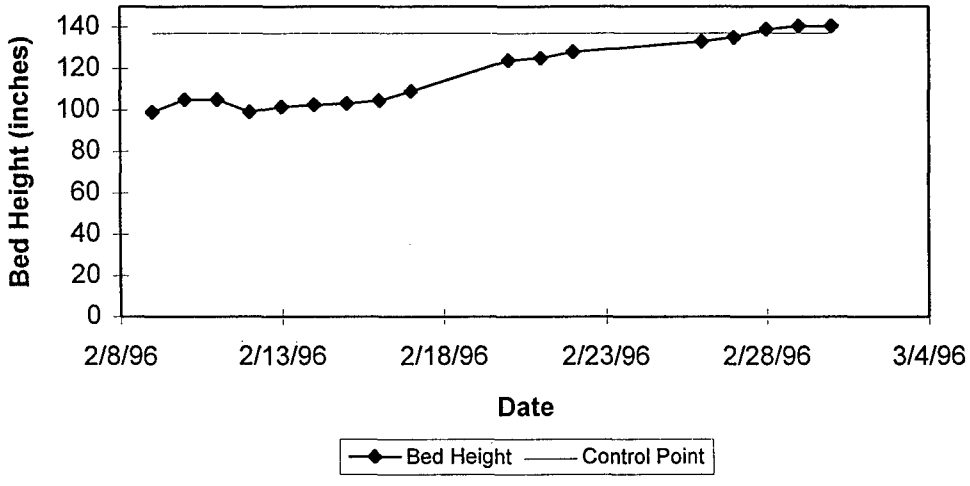


Figure 3-1. Increase in Fluidized Bed Height from Point of Inoculation to Reaching the Growth Control Point.

The removal efficiency for each ketone during the initial 12 days is shown in Figure 3-2. For acetone and MEK, removal efficiency declined rapidly due to the low adsorption capacity of the GAC reaching the lowest point after four days of operation. Removal efficiency improved thereafter, as the biomass population increased. For MIBK, the most readily adsorbed of the ketones tested, removal effectiveness remained above 98.6% throughout this period. By the eleventh day (February 20), effluent concentrations of each of the ketones was below detection limits.

3.4 Steady-State Operational Period #1

The first steady-state operational period, during which system performance was intensively monitored, extended from March 13, 1996 to March 21, 1996. The applied OLR for this period averaged 3.2 Kg COD/m^3-d. The forward feed rate averaged 2.0 gpm, for an empty bed hydraulic residence time (HRT) of 94 minutes. At the end of the period, the reactor was operated at two higher flow rates to examine performance at short HRTs and to confirm that removal efficiency is dependent on applied OLR and not on HRT for the conditions used herein. Removal efficiency was the same at an HRT of 10 minutes as observed at 94 minutes. Performance of the GAC-FBR during this period is summarized below.

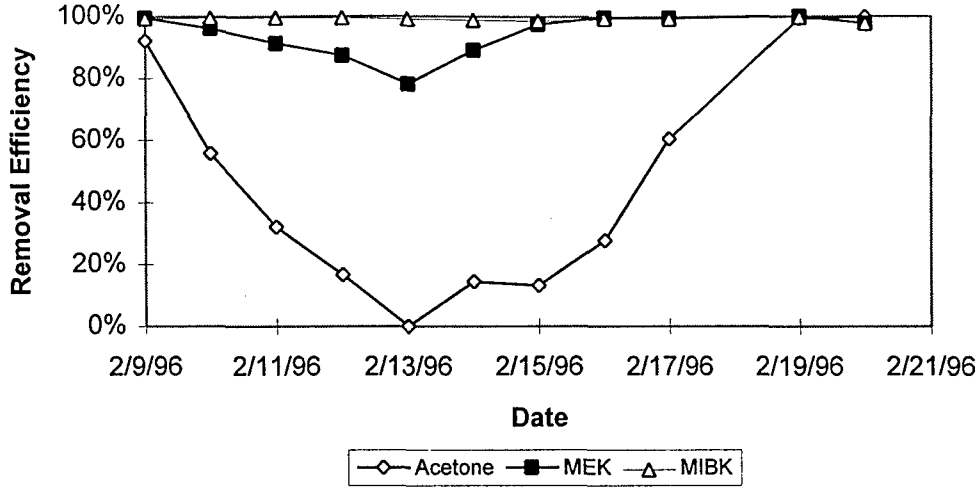


Figure 3-2. Removal Efficiency for Acetone, MEK and MIBK during Start-up of the GAC-FBR.

3.4.1 Ketone Removal Efficiency and Dissolved Oxygen Consumption

During this operational period, the effluent concentration of each of the ketones was always below detection limits. Average influent concentrations for acetone, MEK, and MIBK were 38.5, 25.8, and 21.5 mg/L respectively. Average removal efficiencies were >99.9%, >99.9%, and >99.8% respectively. Detailed results are shown in Tables 3-1 and C-1 (see Appendix C).

Table 3-1. Summary of Results for the GAC-FBR Treating Ketones during Steady-State Period #1.

	Influent (µg/L)	Effluent (µg/L)	% Removal
Acetone	38,500	<26	>99.9
MEK	25,800	<29	>99.9
MIBK	21,500	<43	>99.8
OLR = 3.2 Kg COD/m^3-d; ΔDO/ΔCOD = 0.62 mg/mg; Temperature = 13°C.			

The average COD removed in a single pass through the reactor was ca. 12.2 mg COD/L. The average dissolved oxygen (DO) consumed in a single pass was ca. 7.5 mg/L. The resulting ratio of DO consumed per mg COD removed was 0.62. This is slightly lower than typically experienced when treating petroleum hydrocarbons, but within the normal range of what would be anticipated.

3.4.2 Profiles of Ketone and DO Consumption within the GAC-FBR

As shown in Figure 3-3 (a through c), the average values of four profile sampling events, most of the ketones were removed in the bottom four feet of the bed. The majority of the oxygen was also consumed in this same area at rates commensurate with that required to

oxidize the ketones (Figure 3-3 (d)). This indicates that the reactor has additional capacity for treating considerably higher applied OLRs than the 3.2 Kg COD/m^3-d used for this period.

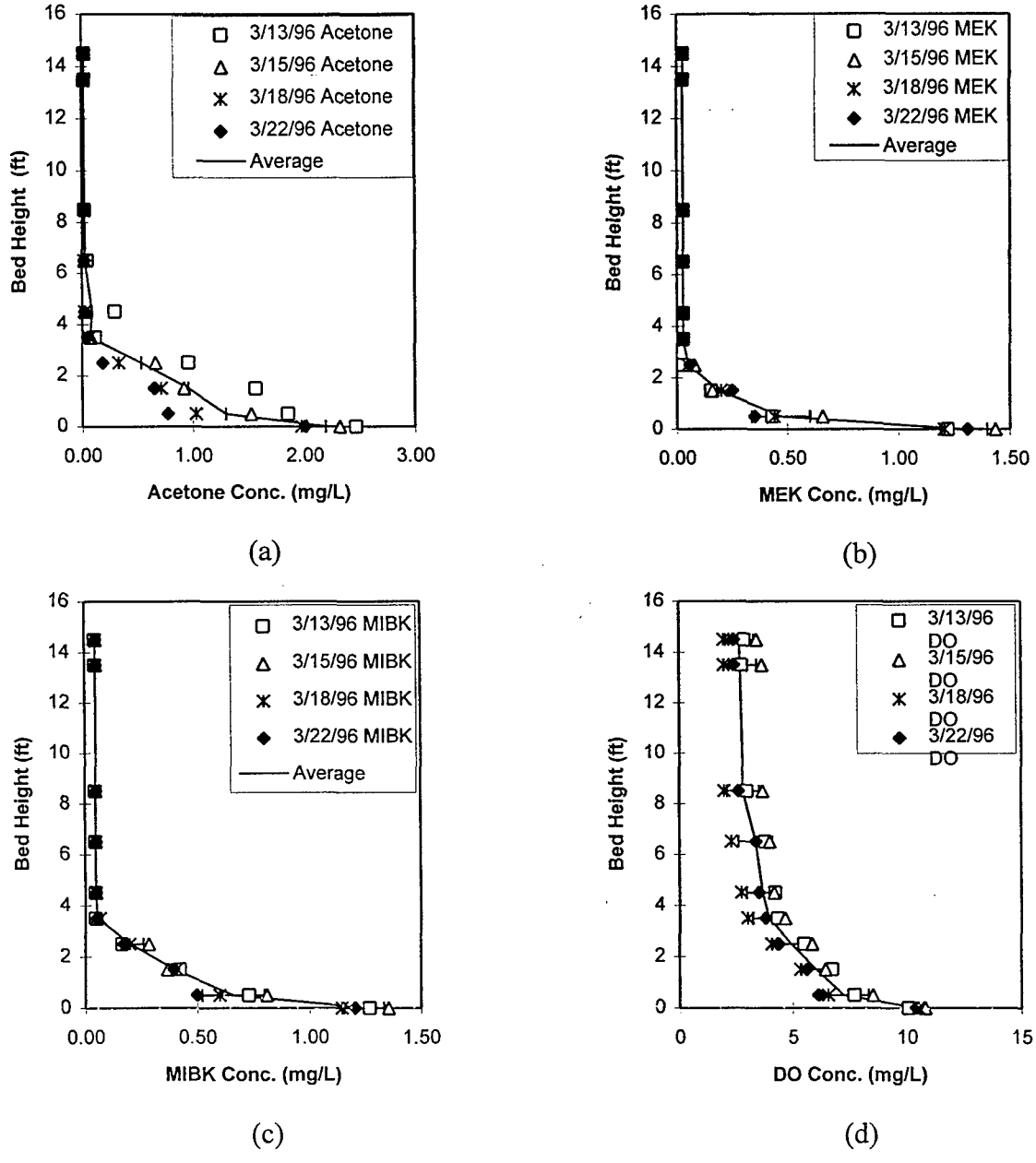


Figure 3-3. Profiles for the GAC-FBR Treating Ketones during the 1st Steady-State Period (a - acetone, b - MEK, c - MIBK, and d - dissolved oxygen).

3.4.3 Biomass on GAC

Samples of the biofilm coated GAC were taken at the end of run 1, over the profile of the GAC-FBR, and analyzed for VSS. The bottom 1 foot of the bed was not well seeded;

VSS concentration was 920 mg/L. The VSS concentration in the remainder of the bed ranged from 10,230 to 11,570 mg/L, resulting in an average biomass concentration in the reactor of 9,070 mg/L.

3.4.4 Effect of Hydraulic Residence Time on Reactor Performance

At the end of Steady-State Period #1, the reactor flow rate was increased to verify that for the range of ketone concentrations examined that ketone removal rates were independent of the hydraulic residence time. The reactor was maintained at each new flow rate for greater than 20 HRTs before sampling, to ensure that representative data was obtained. Flow rates of 11 gpm and 18 gpm yielded empty bed HRTs of 17 and 10 minutes, respectively. Effluent concentrations of each ketone remained below detection limits throughout this period, confirming that ketone removal is independent of HRT for the range of conditions tested. The data for this test are presented in Table 3-2.

Table 3-2. Performance of GAC-FBR at Different HRT and Influent Ketone Concentrations and Constant Applied OLRs of 2.8-3.7 Kg COD/m^3-d.

	HRT = 94 minutes			HRT = 17 minutes			HRT = 10 minutes		
	Influent (µg/L)	Effluent (µg/L)	% Removal	Influent (µg/L)	Effluent (µg/L)	% Removal	Influent (µg/L)	Effluent (µg/L)	% Removal
Acetone	31,380	<26	>99.9	6,420	<26	>99.9	4,540	<26	>99.4
MEK	22,300	<29	>99.6	4,520	<29	>99.4	3,180	<29	>99.1
MIBK	19,500	<43	>99.4	4,300	<43	>99.1	2,940	<43	>99.1

Following completion of this test, the flow rate was reset to 2.0 gpm and the applied OLR was decreased by a factor of ten. The system was allowed to acclimate to this new OLR for two weeks in preparation for the second steady-state period.

3.5 Steady-State Operational Period #2

The second intensively monitored steady-state operational period (#2) was conducted from April 5, 1996 to April 19, 1996. The applied OLR for this period was 0.28 Kg COD/m^3-d, approximately one tenth of the previous loading. The forward feed rate averaged 2.0 gpm, for an empty bed HRT of 94 minutes, the same as for the first steady-state period. Performance of the GAC-FBR during this period is summarized below.

3.5.1 Ketone Removal Efficiency and Dissolved Oxygen Consumption

During this operational period, the effluent concentrations of each of the ketones was always below detection limits. Average influent concentrations for acetone, MEK, and MIBK were 4,000, 1,960 and 1,620 µg/L, respectively. Average removal efficiencies were >99.3%, >98.5%, and >97.2%, respectively, for acetone, MEK and MIBK. Results are summarized in Tables 3-3 and C-2.

Table 3-3. Summary of Results for the GAC-FBR Treating Ketones during Steady-State Period #2.

	Influent (µg/L)	Effluent (µg/L)	% Removal
Acetone	4,000	<26	>99.3
MEK	1,960	<29	>98.5
MIBK	1,620	<43	>97.2
OLR = 0.28 Kg COD/m^3-d; ΔDO/ΔCOD = 1.2; Temperature = 13°C.			

The average COD removed in a single pass through the reactor was 1.2 mg COD/L. The average DO consumed in a single pass was 1.5 mg/L. The resulting ratio of mg of DO consumed per mg COD removed was 1.2. Endogenous respiration was occurring at this low applied OLR. The corresponding decrease in bed height is shown in Figure 3-4.

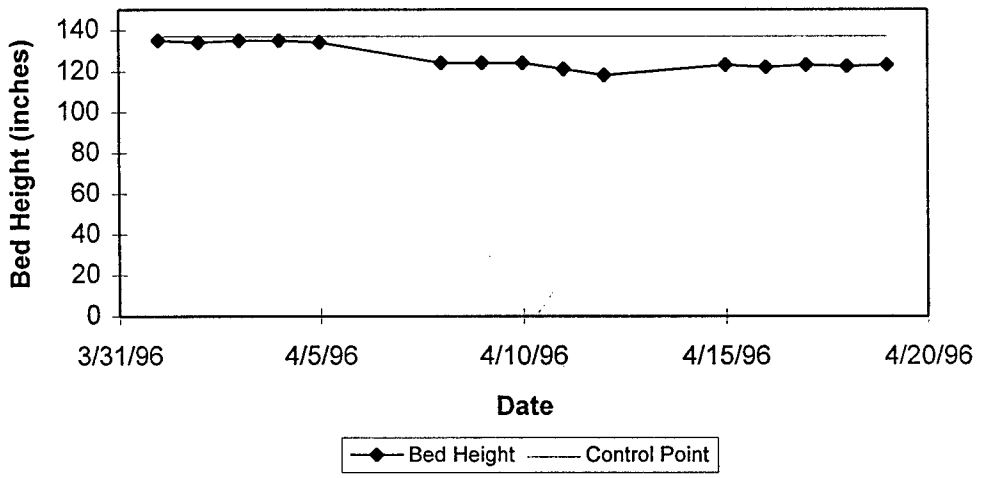


Figure 3-4. Bed Height Response to Reduction from 2.8 to 3.2 Kg COD/^{3}-d Applied OLR.

3.5.2 Ketone and DO Profiles within the GAC-FBR

As shown in Figure 3-5 (a through c), essentially all of the ketones were removed in the bottom two feet of the reactor. The DO consumption profile mirrored the ketone removal in this region (Figure 3-5 (d)). Continued DO consumption, at a slower rate, was observed throughout the remainder of the bed. This indicates some endogenous respiration was occurring in this region.

3.5.3 Biomass on GAC

In addition to the slight decrease in bed height, there was a decrease in the concentration of biomass within the system. Samples were taken through the profile of the FBR and analyzed for VSS concentration immediately at the conclusion of data collection for this steady-state period. A VSS concentration of 2,520 mg/L was observed at one foot above the reactor base. Concentrations at the 3, 5, 7 and 9 foot levels were essentially constant at

an average of 8,990 mg/L. The resulting average biomass concentration in the system was calculated to be ca. 7,600 mg/L, or approximately 83% of what was observed during the 10-fold higher OLR used during the first steady-state period. Taking into account the reduction in bed height, biomass concentration in the system decreased to approximately 71% of that observed at an OLR of ca. 2.8 Kg COD/m^3-d.

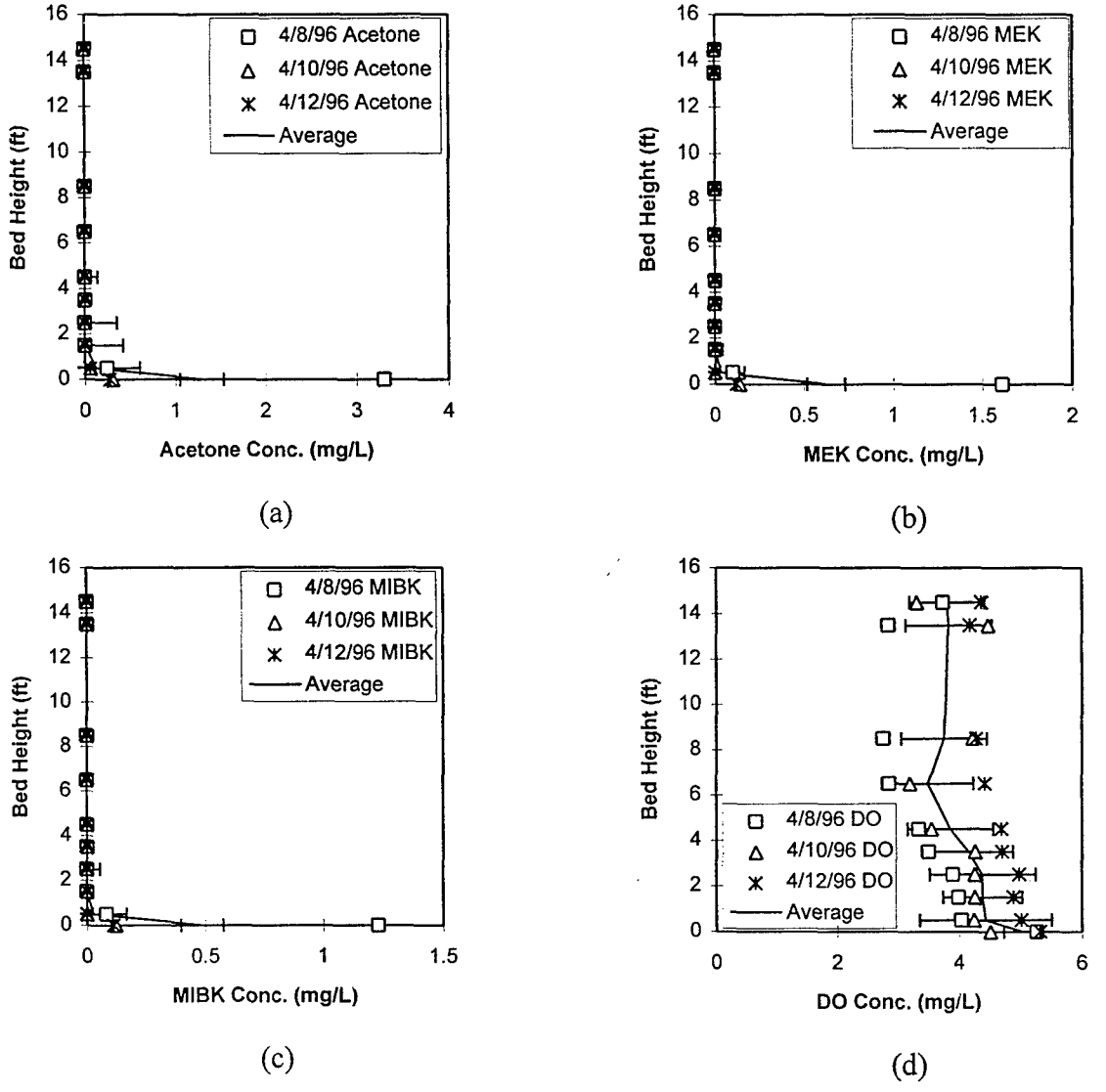


Figure 3-5. Profiles for the GAC-FBR Treating Ketones during the 2nd Steady-State Period (a - acetone, b - MEK, c - MIBK, and d - dissolved oxygen).

3.6 Steady-State Operational Period #3

The third intensively monitored steady-state operational period was conducted from May 6, 1996 to May 23, 1996. The applied OLR for this period was set at 0.039 Kg COD/m3-d, approximately one-eighth of the previous loading. The forward feed rate

averaged 2.9 gpm, for an empty bed HRT of 65 minutes, slightly shorter than for the first two steady-state periods. Performance of the GAC-FBR during this period is summarized below.

3.6.1 Ketone Removal Efficiency and Dissolved Oxygen Consumption

During this operational period, the effluent concentration of each of the ketones was always below detection limits. Average influent concentrations for acetone, MEK, and MIBK were 430, 230, and 210 µg/L, respectively. Average removal efficiencies were >93.5%, >86.5%, and >77.7%, respectively. A summary of results are shown in Tables 3-4 and C-3.

Table 3-4. Summary of Results for the GAC-FBR Treating Ketones during Steady-State Period #3.

	Influent (µg/L)	Effluent (µg/L)	% Removal
Acetone	430	<26	>93.5
MEK	230	<29	>86.5
MIBK	210	<43	>77.7
OLR = 0.037 Kg COD/m^3-d; ΔDO/ΔCOD = 3.5; Temperature = 15°C.			

The average COD removed in a single pass through the reactor was 0.17 mg COD/L. The average DO consumed in a single pass was 0.59 mg/L. The resulting ratio of 3.5 parts DO consumed per part COD removed indicates that significant endogenous respiration was occurring at this very low applied OLR. The corresponding decrease in bed height is shown in Figure 3-6.

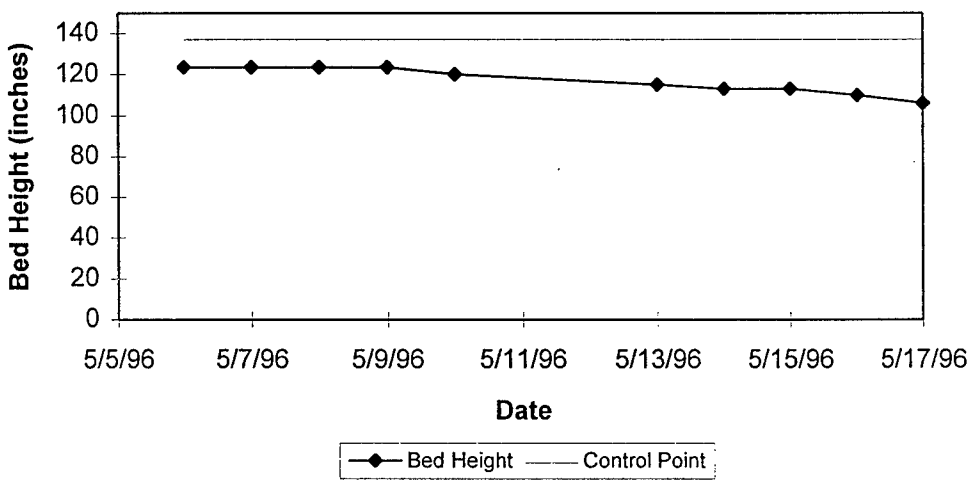


Figure 3-6. Bed Height Response to Reduction from 0.27 to 0.04 Kg COD/m^3-d Applied OLR.

3.6.2 Biomass on GAC

Samples for biomass determination were taken on the final day of this experimental period. The average biomass (VSS) concentration observed was 4,530 mg/L coupled with a 15% decrease in bed height resulted in a reduction in total biomass in the system of approximately 50% that during experimental period with an OLR of 0.28 Kg COD/m^3-d and approximately 35% of that when the OLR was ca. 2.8 Kg COD/m^3-d.

3.7 Biomass Activity Levels

The activity level of the system biomass was examined by removing some biomass (sheared from the GAC carrier particles) and examining the kinetic removal rates for acetone, MEK and MIBK on a mg ketone/mg VSS basis in batch assay tests. A summary of results for biomass samples collected at the end of each of the three steady-state operational periods is presented in Table 3-5 and Figure 3-7. This reduction in biomass concentration indicates significant endogenous respiration and correlates well with the high oxygen consumption to COD removal. Complete assay results are presented in Appendix D.

Table 3-5. Maximum Degradation Rates for Ketones at Three Different Applied Organic Loading Rates.

Loading Rate (Kg COD/m^3-d)	Acetone (mg/mg VSS-min)	MEK (mg/mg VSS-min)	MIBK (mg/mg VSS-min)
2.8	6.22×10^{-5}	9.26×10^{-5}	11.1×10^{-5}
0.28	2.49×10^{-5}	2.98×10^{-5}	3.27×10^{-5}
0.037	0.91×10^{-5}	1.12×10^{-5}	2.02×10^{-5}

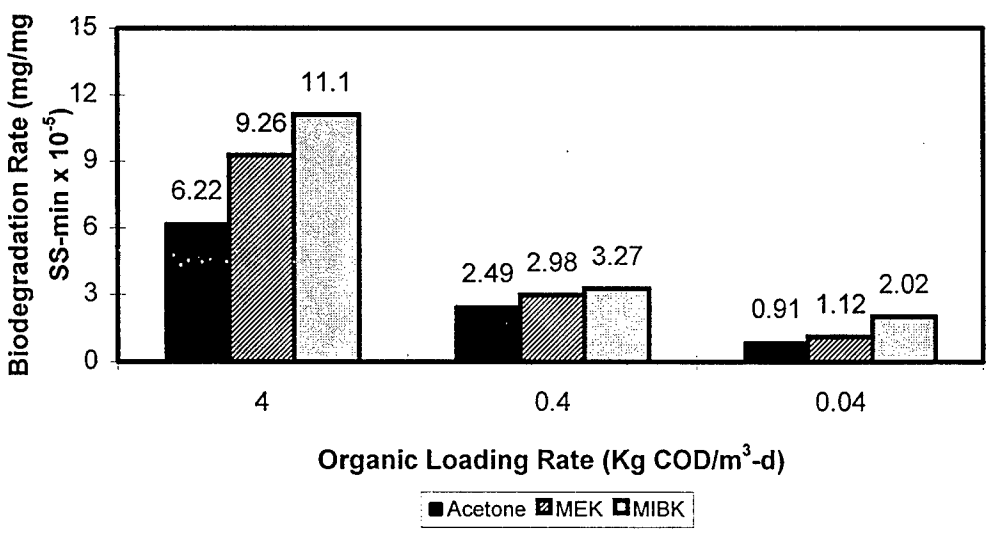


Figure 3-7. Summary Kinetic Experiments with Ketone.

For all three experimental runs, the degradation rates of MEK and MIBK were greater than for acetone despite the fact that acetone concentration was approximately twice that of

the other individual ketones. The rates of degradation in order of fastest to slowest were MIBK > MEK > acetone.

Based on the reduction in ketone degradation rates, in terms of mg substrate per mg biomass (as VSS), and the net change in total biomass in the system during the different OLRs, a net loss of kinetic capacity can be estimated (Table 3-6).

Table 3-6. Relative Kinetic Capacity for Oxidation of Acetone, MEK and MIBK due to Decreases in the applied Organic Loading Rates (OLR).

	Relative Kinetic Capacity		
OLR (Kg COD/m^3-d)	Acetone	MEK	MIBK
3.2	1.0	1.0	1.0
0.28	0.28	0.23	0.21
0.037	0.05	0.04	0.06

A decrease of 3.6 to 4.8-fold capacity in acetone and MIBK, respectively, was observed when the OLR was decreased 11-fold from ca. 3.2 to 0.28 Kg COD/m^3-d. When the OLR was again decreased 7.5-fold to 0.037 Kg COD/m^2-d, the net kinetic capacity decreased by any where from 3.5 to 5.8-fold. Overall, a 86-fold reduction in OLR resulted in an approximate 20-fold reduction in kinetic capacity within the GAC-FBR system for all three ketones.

3.8 Estimation of Coefficients of Oxygen Utilization

Based on system biomass concentrations, and net oxygen and COD mass, removal per pass through the GAC-FBR system, an estimate of the coefficients of oxygen utilization can be made. It is understood that because this is a biofilm and not suspended growth system, the normal equations used for activated sludge systems do not precisely apply, especially if there are thick biofilms and anoxic/anaerobic inner zones. The biofilms used in this study were purposely kept quite thin (maximum 50 to 100 μm), therefore although not completely accurate, some estimate of the coefficients of oxygen utilization was made.

Oxygen consumption can be written as follows:

$$\frac{dO_2}{dt} = a' \frac{dS}{dt} + b' X \qquad \textbf{(3-1)}$$

where S is substrate concentration (as COD), X is the average biomass concentration (mg SS/L), (a') is the oxygen required per mass of COD removed (mg/mg) and (b') is the decay coefficient (day^{-1}).

Using the three steady-state data sets, all the information needed for estimating a' and b' is available (Table 3-7).

Table 3-7. Data from Steady-State Periods.

OLR (Kg COD/m^3-d)	VSS (mg/L)	Δ COD (mg/L)	Δ DO (mg/L)	HRT* (min)
3.2	9,070	12.2	7.5	6.25
0.28	7,600	1.2	1.5	5.35
0.037	4,530	0.17	0.59	4.55
*based on flow rate and measured bed height (empty bed retention time)				

A plot of $\frac{dS/dt}{X}$ $vs.$ $\frac{dO_2/dt}{X}$ can be used to simultaneously estimate a' and b'. A linear regression of the data yields a' as the slope and b' as the intercept. The values obtained from this analysis are:

a' = 0.51 (mg/mg)
b' = 0.033 (day^{-1})

An r^2 of >0.999 was obtained, indicating a good fit of the data.

The measured versus calculated oxygen consumptions per pass through the GAC-FBR for all three steady-state periods is presented in Table 3-8. Calculated results compare well with measured values. Results indicate that endogenous respiration accounted for more than half of the oxygen used during the steady-state periods at OLRs of 0.28 and 0.037 Kg COD/m^3-d.

Table 3-8. Actual and Calculated Oxygen Consumption for the Different Steady-State Periods.

	Calculated Oxygen Consumption		
Actual	Oxidation	Endogenous Respiration	Total
7.5	6.22	1.23	7.45
1.5	0.61	0.93	1.54
0.59	0.087	0.472	0.56

4. ECONOMIC ANALYSIS

In order to obtain an estimate of the cost of treating ketones in groundwater, flow rates of 30-350 gpm at a total influent COD of 40-45 mg/L were examined and the resultant operational and capital costs estimated (see Appendix E for example). Power costs were calculated at $0.06/kwh. Manpower was estimated at 10% of a $30,000 operation per year or $3,000/year. Capital was amortized over 10 years at a 5% discount rate. Results are presented in Table 4-1. For 350 gpm, the cost per 1000 gallons treated was $0.27/1000 gal. This increased to $0.41/1000 for 150 gpm and up to $1.33/1000 gal at 30 gpm of flow. High ketone concentrations would affect primarily the cost associated with chemicals and power. Higher flow rates would reduce the overall cost of treatment per 1000 gallon while for flows less than 30 gpm the overall cost per 1000 gallons would increase.

Table 4-1. Cost of Treating Ketones in Groundwater using an Aerobic GAC-FBR System.

Flow (gpm)	Chemicals and Power ($/yr)	Manpower ($/yr)	Total* ($/yr)	Total ($/1000 gal)
30	1009	3000	20,993	1.33
150	3997	3000	32,812	0.41
350	7429	3000	49,152	0.27

*Includes amortization of capital at 10 years and a 5% discount rate.

5. SUMMARY AND CONCLUSIONS

A four-month demonstration was conducted using the GAC-FBR process to aerobically treat ketones (acetone, MEK and MIBK) at organic loading rates (OLR) ranging from a high of 3.2 Kg COD/m^3-d to 0.037 Kg COD/m^3-d. The objectives were to 1) demonstrate that ketones, compounds difficult to treat using air stripping or carbon adsorption, can be readily degraded to below detection limits at a range of inlet concentrations and OLR, and 2) to demonstrate that the process remains viable even at extremely low OLRs. The primary conclusions that can be drawn from this effort include:

- Acetone, MEK and MIBK could be consistently reduced in concentration by >99%. Effluent concentrations were well below regulatory limitations and, in general, below the method detection limits.

- The rates of degradation observed from highest to lowest were MIBK > MEK > acetone.

- An 86-fold reduction in applied mass loading of ketones per unit volume per day from typical Organic Loading Rates (OLRs) of 3.2 Kg COD/m^3-d to 0.037 Kg COD/m^3-d, resulted in a 20-fold decrease in net kinetic capacity for degradation of acetone, MEK and MIBK in the aerobic GAC-FBR.

- The remaining biomass population still possessed the capacity to degrade 4.4 (acetone) to 20 (MIBK) times more mass of ketones than was fed at this OLR rate, indicating considerable excess capacity.

- The cost of treatment using the GAC-FBR appears quite reasonable, ranging from $0.27 to $1.33 ($/1000 gallons) for 30 to 350 gpm, and a total COD of 43 mg/L and a groundwater temperature of 10°C.

Appendix A

Daily Checklist for Ketone Reactor

Experimental stage: _____

Parameter	Location	Units	Range	Mon	Tues	Wed	Thurs	Fri	Sat	Sun
Day #										
Date:										
Time:										
Operator:										
NUTRIENT SYSTEM										
Percent Stroke Length	Dial on pump face	%	30-100							
Percent Stroke Rate	Dial on pump face	%	10-100							
Nutrient Feed Tank Level	Use dip stick	gal	3-25							
AIR-SEP SYSTEM										
Oxygen tank regulator pressure	Gauge on tank outlet	psig	43-48							
Feed air pressure	Top of Air-Sep	psig	90-150							
Max cycle pressure	Top of Air-Sep	psig	65-70							
Oxygen receiver pressure	Top of Air-Sep	psig	45-60							
CONTROL PANEL (circle appropriate setting, normal setting shown)										
Influent flow	panel	GPM	0-32							
Reactor flow	panel	GPM	28-32							
Influent pH	panel	su	6-8							
Influent DO	panel	mg/L	2-40							
Effluent pH	panel	su	6-8							
Effluent DO	panel	mg/L	2-3							
Effluent Temperature	panel	C	6-15							
Pump Select	Switch Setting	1/2	1	1 2	1 2	1 2	1 2	1 2	1 2	1 2
Fluidization Pump	Switch Setting	Man/Off/Auto	Auto	M O A	M O A	M O A	M O A	M O A	M O A	M O A
Nutrient Pump Running	Switch Setting	Man/Off/Auto	Auto	M O A	M O A	M O A	M O A	M O A	M O A	M O A
" " "	Light On?	On/Off	On	On Off	On Off	On Off	On Off	On Off	On Off	On Off
pH Pump	Switch Setting	Man/Off/Auto	Auto	M O A	M O A	M O A	M O A	M O A	M O A	M O A
Mixer Running	Light On?	On/Off	On	On Off	On Off	On Off	On Off	On Off	On Off	On Off
pH SYSTEM										
Percent Stroke Length	Dial on pump face	%	30-100							
Percent Stroke Rate	Dial on pump face	%	10-100							
pH Feed Tank Level	Use dip stick	gal	3-25							
KETONE SYSTEM										
Percent Stroke Length	Dial on pump face	%	30-100							
Percent Stroke Rate	Dial on pump face	%	10-100							
Ketone Mix Tank Level	Use dip stick	in	3-55							
Totalizer Meter Reading	meter	gallons								
AIR COMPRESSOR										
Turn control panel switch to Off	Control panel									
Oil level	Dip stick	-								
Turn switch back to Auto	Control panel									
Tank Pressure	Gauge on tank front	psig	90-150							
REACTOR PIPING										
Reactor inlet pressure	gauge after strainer	psig	7-9							
Fluid. pump discharge pressure	gauge after pump	psig	34-40							
Eductor inlet pressure	gauge above bubble trap	psig	25-40							

Daily Checklist for Ketone Reactor

Experimental stage: _____

Day #															
Date:															
Time:															
Operator:															
Parameter	Location	Units	Range	Mon		Tues		Wed		Thurs		Fri		Sat		Sun	
CARBON BED HEIGHT (mixer off, check distance from top of reactor flange to bed, count 6"/knot, turn mixer back on)																	
Carbon bed height	depth gauge	in															
Mixer on	panel switch/light	On/Off	On	On	Off	On	Off	On	Off	On	Off	On	Off	On	Off	On	Off
MEASURED VALUES																	
Influent DO		mg/L															
Influent temperature		degrees C															
Reactor Influent		mg/L															
Effluent		mg/L															
Clean influent DO probe						X						X					
make up nutrients						X											
make up ketone solution						X											
check strainer baskets						X											
check pH probe calibration						X											
Start-up																	
ketones				X		X		X		X		X					
Reactor profiles (DO, ketones)								X									
SS/VSS								X									
nitrogen, phosphorous								X									
Acclimation periods																	
ketones				X				X				X					
Reactor profiles (DO, ketones)								X									
SS/VSS								X									
nitrogen, phosphorous								X									
Campaign periods																	
ketones				X		X		X		X		X					
Reactor profiles (DO, ketones, biomass on GAC)				X				X				X					
SS/VSS				X		X		X		X		X					
nitrogen, phosphorous				X		X		X		X		X					

Appendix B

KETONES BY STATIC HEADSPACE SAMPLING- GC/FID ANALYSIS

1. SCOPE AND APPLICATION

This method has been used to quantitatively analyze the following compounds in aqueous samples:

- Acetone
- Methyl Ethyl Ketone
- Methyl Isobutyl Ketone

This method is also used for the fractionation of petroleum hydrocarbons by boiling point (Simulated Distillation, SIMDIS), quantified in benzene equivalents for BPs ranging from <69°C to >252°C.

2. SUMMARY OF METHOD

This method provides gas chromatographic conditions and headspace analyzer settings for the detection of ketones in aqueous samples. Capillary columns, temperature programs and an flame ionization detector (FID) are used in this method.

3. INTERFERENCES

Samples can be contaminated by diffusion of volatile organic compounds (VOCs) during sampling, shipping and sample storage. Refer to the QA/QC section to check for such contamination.

4. APPARATUS AND MATERIALS

Gas Chromatograph. A Varian 3600 GC is used for this analysis. The GC hardware includes a septum-equipped programmable on-column injector (SPI), direct capillary interface heated transfer line from the headspace analyzer, input and output relays for data acquisition and 10,000 mV signal outputs for the data acquisition system.

Columns. A 60 m VOCOL capillary column (Supeico), 0.53 mm I.D. and 3.0 µm d_f is used.

Detector. A capillary FID, with a ceramic tip, is used.

Sample Introduction. Via a heated capillary transfer line from a static headspace autosampler. Autosampler is equipped with a 50-sample carrousel, where samples are held at ambient temperature. A 12-position platen allows for vials to be heated simultaneously, for sequencing sample introduction back-to-back, while maintaining constant heating time.

Syringes. Hamilton and Unimetrics Luerlok gas-tight syringes are used for transfer of solutions containing volatile components.

Glassware. 20 mL crimp top headspace sampler vials are used, with Teflon-coated septa.

Microsyringes. Gas tight Hamilton and Unimetrics 10, 25, 50 and 100 µL Microliter syringes are used.

Analytical Balance. 0.0001 g.

Data Acquisition and Analysis. A Windows based chromatographic data acquisition system, PE-Nelson Turbochrom 3.0, is used. The system is interfaced to the GC via a 900-Series A/D link box, to provide for continuous storage of raw chromatograms in a PC, for subsequent off-line batch analysis.

5. REAGENTS

Stock Standards. Methanolic stock solutions are procured from Supelco, Inc. These Supelco standards are only used for the lower end of the calibration curve. We also made up our own standard for the higher end of the curve. Our standards were made from 8 grams each of Acetone, Methyl Ethyl Ketone and Methyl Isobutyl Ketone per liter of Nano-pure water. Smaller amounts were placed into I-chem vials and frozen for future use. These were used for calibration during routine analyses.

Aqueous Calibration Standards. These are prepared in organic-free reagent water, on the day of analysis.

Reagent Water. Nano-pure water is prepared in-house, following a double distillation of building water.

6. SAMPLE COLLECTION, PRESERVATION AND HANDLING

All samples were taken in house. Samples are taken from an effluent and an influent sample port. Duplicate sub-samples of 10 mL each are subject to GC analysis from each syringe drawn. The samples are taken with an all glass, 20 mL syringe. The syringe is rinsed with deionized water before sampling and prerinsed with sample prior to withdrawal of the sub-sample volume. The samples are then split into two 20 mL headspace vials and sealed using Teflon coated septa and aluminum crimp cap seals. The samples are stored at 4°C for no longer than 7 days before analysis.

7. PROCEDURE

Summary

VOCs are introduced into the GC using a static headspace autosampler. This method is used directly on groundwater samples and low-concentration aqueous process effluents. A salting-out procedure is used to increase the precision of the method for all volatile components. Residue analysis grade NaCl (7 gms) is used in each 20 mL headspace vial, for a 10 mL aqueous sample.

Recommended Headspace Sampler Conditions. The following are the settings for the Genesis:

Platen Temperature:	80
Platen Equilibrium:	0 min
Sample Equilibrium:	60 min
Vial Size:	20 mL
Mixer:	OFF
Pressurize:	0.4 min
Loop Fill:	0.15 min
Loop Inject:	0.3 min
Pressure Equilibrium:	0.2 min
Loop Equilibrium:	0.2 min
Valve Temperature:	150
Line Temperature:	210
Injections Per Vial:	1
GC Cycle Time:	17 min
Parameter Optimization:	OFF
Transfer Line Back pressure:	14 psi

Recommended GC Conditions. The following are the setting for the heated zones:

Injector Temperature:	250
Column Head Pressure (from transfer line):	14 psi
Initial Column Temperature:	45
Initial Column Hold Time:	0 min
Program 1 Final Column Temperature:	150
Program 1 Column Hold Time:	0 min
Detector Temperature:	250
FID Attenuation:	1
FID Range:	10^{12}
FID AutoZero:	ON
Time Program FID:	NO

Calibration. Five to seven-level calibration curves were generated for individual components, in concentrations ranging from 1.57 mg/L to 100 mg/L. Linear regression with forced origin was used to calculate the calibration factors. SIMDIS fractions are calibrated in benzene equivalents.

GC Analysis. The following are representative retention times for individual components:

Compound	*RT (min)*
Acetone	3.13
Methyl Ethyl Ketone	4.22
Methyl Isobutyl Ketone	6.26

Method Detection Limits. Detection limits are established periodically, by analyzing the standard deviation of response to 7 replicates of a very low level standard. The following detection limits (DL) are for these compounds.

Compound	MDL (ppm)
Acetate	0.0256
MEK	0.0287
MIBK	0.0425

Estimated Quantitation Limits. Quantitation limits are established for new sample matrices by the analysis of variance in replicates spiked with low level standards.

8. REFERENCES

- Optimization of Parameters in Static Headspace GC, Varian Application Note GC40:1291
- Design and Performance of an Automatic Static Headspace Analyzer, Tekmar, 41st Pittcon, 1990.
- The Effect of Mixing on Liquid Samples in Static Headspace Analysis, Tekmar, Pittcon, 1990.
- Varian Genesis Headspace Autosampler, Doc. # 802824-002
- Model 3600 Gas Chromatograph, Doc. # 802838-003
- Gas Analysis by Headspace-Gas Chromatography... HP Application Note 228-248
- Performing USP Method <467> Using the HP 7694 Headspace Sampler, HP Application Note 228-237
-

BIOMASS ON CARBON

1. Take 40 ml of wet carbon (usually triplicates).
2. Label your flasks (250 ml).
3. Weigh flasks and record weights.
4. Make a sample log data sheet.
5. Always remember to use the same balance once your experiment has begun.
6. After placing samples in vacuum oven, the vacuum pressure should not exceed -10. It should stay around -5.
7. Keep in oven over night (12-24 hours).
8. Cool to room temperature and weigh. (Carbon + Flask + Biomass)= weight.
9. Add 100 ml of 4M NaOH.
10. *Take 160.0g NaOH pellets and dissolve in 1L of distilled water.
11. Decant NaOH into each flask and cap with parafilm.
12. Give parafilm a small twist to make sure it is snug. So it doesn't leak.
13. Place samples on shaker in room C129. Set both temperatures to 90 degrees and shaker speed to 1500.
14. Shake for 24 hours.
15. Decant off NaOH carefully not to lose any of the floating carbon.
16. Always decant into another container (not the sink).
17. Rinse carbon until the water is clear.
18. Put back in oven (105) overnight.
19. Weigh again after cooling (second dry weight) Carbon + Flask - Biomass.
20. Watch for fines - which is a small film covering the top of the water.

*Note if fines are present on data sheet.

TOTAL AND VOLATILE SUSPENDED SOLIDS

Total Solids

1. Pre-weigh all pans before beginning.
2. Take triplicate samples of 20 to 50 mL depending on the amount of sample available.
3. Place the pans with the samples into a vacuum oven for approximately 24 hours.
4. Remove samples and allow them to cool in a dessicator for about 1 hour.
5. Reweigh the samples with the same balance. You now can subtract the initial weight from the finally weight. This gives you the total solids.

Total Volatile Solids

1. Continuing on from the total solids, place the samples into an ashing oven for two hours.
2. Remove from oven and allow to cool.
3. Reweigh the samples, again with the same balance. You can now subtract the initial weight from the finally weight. This gives you the total volatile solids.

Total Suspended Solids

1. Pre-weigh filter papers and pans.
2. Place filter paper in suction funnel, wet with deionized water to form a seal.
3. Again place between 20 and 50 mL into the suction funnel depending on the amount of sample available and the amount of sample used for total solids if using for total dissolved solids.
4. Let funnel pull all of the sample through the paper and remove. Place the paper into the pre-weighed pans.
5. Place the pans with samples into vacuum oven for 24 hours.
6. Remove samples and allow to cool.
7. Weigh samples with the same balance. You can now subtract the initial weight from the finally weight. This gives you the total suspended solids.

Volatile Suspended Solids

1. Continuing on from the total suspended solids, place the samples into an ashing oven for two hours.
2. Remove from oven and allow to cool.
3. Reweigh the samples, again with the same balance. You can now subtract the initial weight from the finally weight. This gives you the volatile suspended solids.

Total Dissolved Solids

1. You can either get this from taking your total solids and subtracting your total suspended solids or you may save the sample that was pulled through the filter paper and dry and weigh this as before.
2. This will give you your total dissolved solids.

Volatile Dissolved Solids

1. Continuing on from the total dissolved solids, place the samples into an ashing oven for two hours.
2. Remove from oven and allow to cool.
3. Reweigh the samples, again with the same balance. You can now subtract the initial weight from the finally weight. This gives you the volatile dissolved solids.

Appendix C

Table C-1. Performance data for the GAC-FBR during steady-state operational period #3.

	ACETONE (mg/L)				MEK (mg/L)				MIBK (mg/L)			
Date	Influent	Reactor Influent	Effluent	% Removal	Influent	Reactor Influent	Effluent	% Removal	Influent	Reactor Influent	Effluent	% Removal
5/6/96	0.46	0.03	BDL	94.35%	0.23	BDL	BDL	87.83%	0.24	BDL	BDL	82.50%
5/7/96	0.43	0.03	BDL	93.95%	0.22	BDL	BDL	87.27%	0.21	BDL	BDL	80.00%
5/8/96	0.47	0.03	BDL	94.47%	0.24	BDL	BDL	88.33%	0.22	BDL	BDL	80.91%
5/9/96	0.52	0.03	BDL	95.00%	0.28	BDL	BDL	90.00%	0.26	BDL	BDL	83.85%
5/10/96	0.50	0.02	BDL	94.80%	0.25	BDL	BDL	88.80%	0.22	BDL	BDL	80.91%
5/13/96	0.50	0.02	BDL	94.80%	0.27	BDL	BDL	89.63%	0.24	BDL	BDL	82.50%
5/14/96	0.40	0.03	BDL	93.50%	0.22	BDL	BDL	87.27%	0.22	BDL	BDL	80.91%
5/15/96	0.43	0.02	BDL	93.95%	0.22	BDL	BDL	87.27%	0.19	BDL	BDL	77.89%
5/16/96	0.41	0.03	BDL	93.66%	0.22	BDL	BDL	87.27%	0.21	BDL	BDL	80.00%
5/17/96	0.53	0.03	BDL	95.09%	0.29	BDL	BDL	90.34%	0.25	BDL	BDL	83.20%
5/20/96	0.27	0.05	BDL	90.37%	0.14	BDL	BDL	80.00%	0.11	BDL	BDL	61.82%
5/21/96	0.24	0.03	BDL	89.17%	0.12	BDL	BDL	76.67%	0.11	BDL	BDL	61.82%
5/22/96	0.25	0.04	BDL	89.60%	0.13	BDL	BDL	78.46%	0.12	BDL	BDL	65.00%
5/23/96	0.62	0.04	BDL	95.81%	0.33	BDL	BDL	91.52%	0.30	BDL	BDL	86.00%
average	0.43	0.03		93.47%	0.23			86.48%	0.21			77.66%
std dev	0.11	0.01		2.14%	0.06			4.63%	0.06			8.28%

BDL = Below detection limits.

Table C-2. Performance data for the GAC-FBR during steady-state operational period #2.

	ACETONE (mg/L)				MEK (mg/L)				MIBK (mg/L)			
Date	Influent	Reactor Influent	Effluent	% Removal	Influent	Reactor Influent	Effluent	% Removal	Influent	Reactor Influent	Effluent	% Removal
4/5/96	3.67	0.24	BDL	99.29%	1.67	0.12	BDL	98.32%	1.35	0.10	BDL	96.89%
4/8/96	3.30	0.24	BDL	99.21%	1.61	0.10	BDL	98.26%	1.23	0.08	BDL	96.59%
4/9/96	2.85	0.23	BDL	99.09%	1.34	0.11	BDL	97.91%	0.87	0.07	BDL	95.17%
4/10/96	4.45	0.30	BDL	99.42%	2.29	0.14	BDL	98.78%	1.72	0.12	BDL	97.56%
4/11/96	4.81	0.30	BDL	99.46%	2.47	0.15	BDL	98.87%	1.93	0.12	BDL	97.82%
4/12/96	4.71	0.27	BDL	99.45%	2.27	0.12	BDL	98.77%	1.90	0.11	BDL	97.79%
4/16/96	3.56	0.27	BDL	99.27%	1.72	0.12	BDL	98.37%	1.58	0.11	BDL	97.34%
4/18/96	4.25	0.32	BDL	99.39%	2.03	0.15	BDL	98.62%	1.84	0.15	BDL	97.72%
4/19/96	4.37	0.28	BDL	99.41%	2.28	0.14	BDL	98.77%	2.17	0.14	BDL	98.06%
average	4.00	0.27		99.33%	1.96	0.13		98.52%	1.62	0.11		97.22%
std dev	0.68	0.03		0.12%	0.39	0.02		0.32%	0.41	0.03		0.90%

BDL = Below detection limits.

Table C-3. Performance data for the GAC-FBR during steady-state operational period #1.

	ACETONE (mg/L)				MEK (mg/L)				MIBK (mg/L)			
Date	Influent	Reactor Influent	Effluent	% Removal	Influent	Reactor Influent	Effluent	% Removal	Influent	Reactor Influent	Effluent	% Removal
3/13/96	38.00	2.47	BDL	>99.93%	22.12	1.22	BDL	>99.87%	20.70	1.27	BDL	>99.80%
3/14/96	53.32	2.78	BDL	>99.95%	38.00	1.80	BDL	>99.93%	26.08	1.75	BDL	>99.84%
3/15/96	46.36	2.32	BDL	>99.94%	32.52	1.44	BDL	>99.91%	24.78	1.36	BDL	>99.83%
3/18/96	33.30	1.97	BDL	>99.92%	24.14	1.21	BDL	>99.88%	21.54	1.15	BDL	>99.81%
3/19/96	35.34	2.12	BDL	>99.93%	24.48	1.42	BDL	>99.89%	21.40	1.32	BDL	>99.80%
3/20/96	34.96	2.01	BDL	>99.93%	24.46	1.31	BDL	>99.89%	20.86	1.21	BDL	>99.80%
3/21/96	31.38	2.11	BDL	>99.92%	22.30	1.43	BDL	>99.87%	19.50	1.32	BDL	>99.78%
3/22/96	35.54	2.89	BDL	>99.93%	18.64	1.28	BDL	>99.85%	17.02	1.37	BDL	>99.75%
average	38.5	2.33		>99.93%	25.8	1.39		>99.89%	21.5	1.34		>99.80%
std dev	7.5	0.35		0.02%	6.3	0.19		0.02%	2.9	0.18		0.02%

BDL = Below detection limits

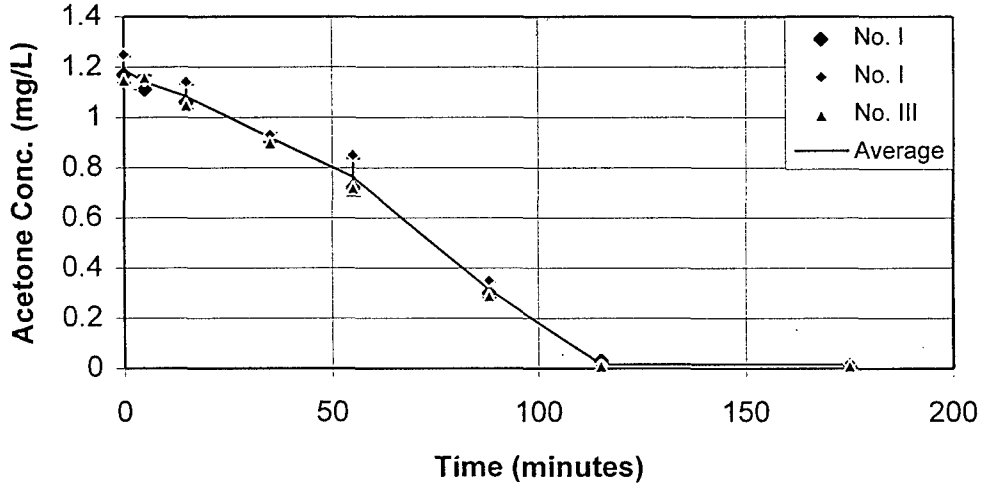
Appendix D

Ketone Kinetic Experiment ---- Acetone Degradation

Date: 4/1/96 SS: 0.222 g/L 0.908
Operator: Jing Shi VSS: 0.201 g/L

Time (minutes)	No. I Acetone	No. II Acetone	No. III Acetone	Average	std
0	1.17	1.25	1.15	1.19	0.05
5	1.11	1.15	1.16	1.14	0.03
15	1.06	1.14	1.05	1.08	0.05
35	0.93	0.93	0.9	0.92	0.02
55	0.72	0.85	0.72	0.76	0.08
88	0.3	0.35	0.29	0.31	0.03
115	0.03	0.01	0.01	0.02	0.01
175	0.02	0.02	0.01	0.02	0.01

Acetone Degradation Chart



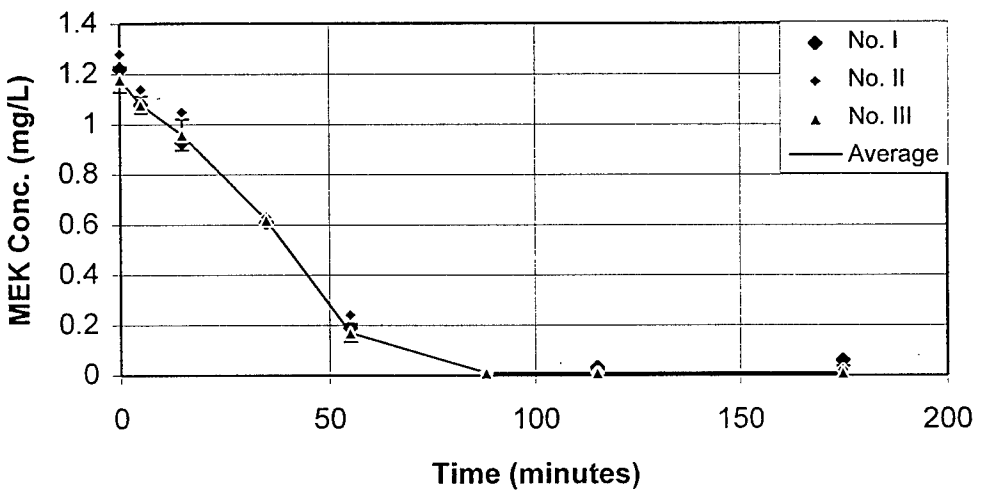
Estimated degradation rate: 6.22×10^{-5} 1/min.

Ketone Kinetic Experiment ---- MEK Degradation

Date: 4/1/96 SS: 0.222 g/L 0.908
Operator: Jing Shi VSS: 0.201 g/L

Time (minutes)	No. I MEK	No. II MEK	No. III MEK	Average	std
0	1.22	1.28	1.18	1.18	0.05
5	1.08	1.14	1.08	1.08	0.03
15	0.93	1.05	0.96	0.96	0.06
35	0.61	0.63	0.62	0.62	0.01
55	0.19	0.24	0.17	0.17	0.04
88		0.01	0.01	0.01	0.00
115	0.03	0.01	0.01	0.01	0.01
175	0.06	0.02	0.01	0.01	0.03

MEK Degradation Chart



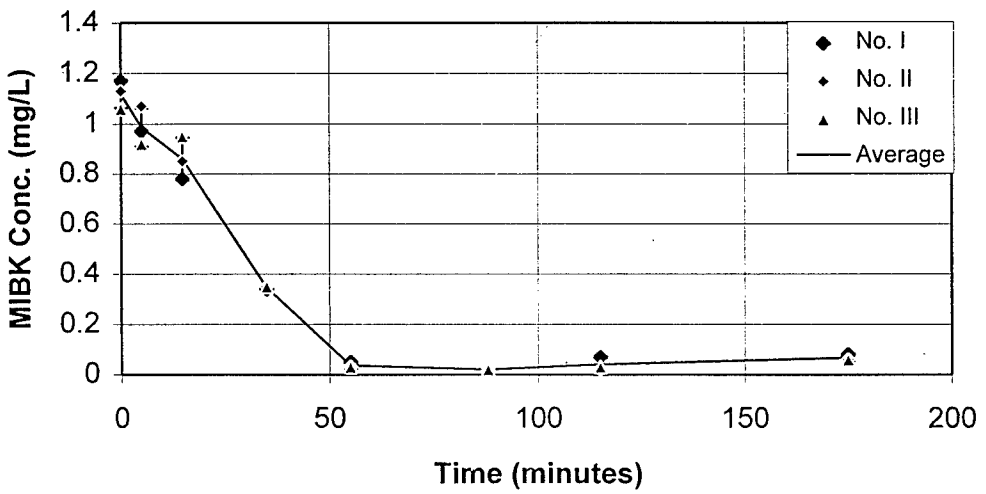
Estimated degradation rate: 9.26×10^{-5} 1/min.

Ketone Kinetic Experiment ---- MIBK Degradation

Date:	4/1/96	SS:	0.222 g/L	0.908
Operator:	Jing Shi	VSS:	0.201 g/L	

Time (minutes)	No. I MIBK	No. II MIBK	No. III MIBK	Average	std
0	1.17	1.13	1.06	1.12	0.06
5	0.97	1.07	0.92	0.99	0.08
15	0.78	0.85	0.95	0.86	0.09
35	0.34	0.35	0.35	0.35	0.01
55	0.05	0.03	0.03	0.04	0.01
88		0.02	0.02	0.02	0.00
115	0.07	0.02	0.03	0.04	0.03
175	0.08	0.06	0.06	0.07	0.01

MIBK Degradation Chart



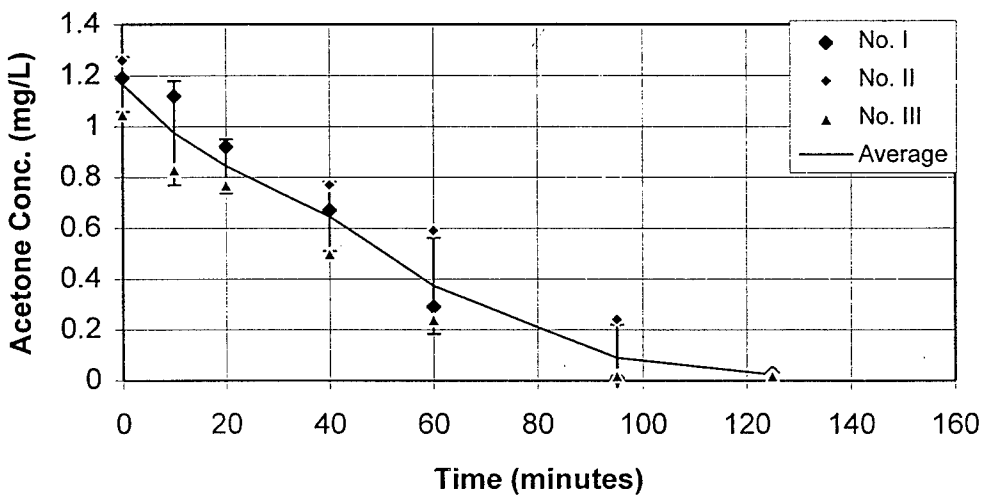
Estimated degradation rate: 11.1×10^{-5} 1/min.

Ketone Kinetic Experiment ---- Acetone Degradation Rate in 1/10 Loading

Date: 4/30/96 SS: 0.527 g/L 0.93
Operator: Jing Shi VSS: 0.490 g/L

Time (minutes)	No. I Acetone	No. II Acetone	No. III Acetone	Average	std
0	1.19	1.26	1.05	1.17	0.11
10	1.12		0.83	0.98	0.21
20	0.92		0.77	0.85	0.11
40	0.67	0.77	0.5	0.65	0.14
60	0.29	0.59	0.24	0.37	0.19
95	0.01	0.24	0.02	0.09	0.13
125	0.03	0.02	0.02	0.02	0.01
150					

Acetone Degradation Chart



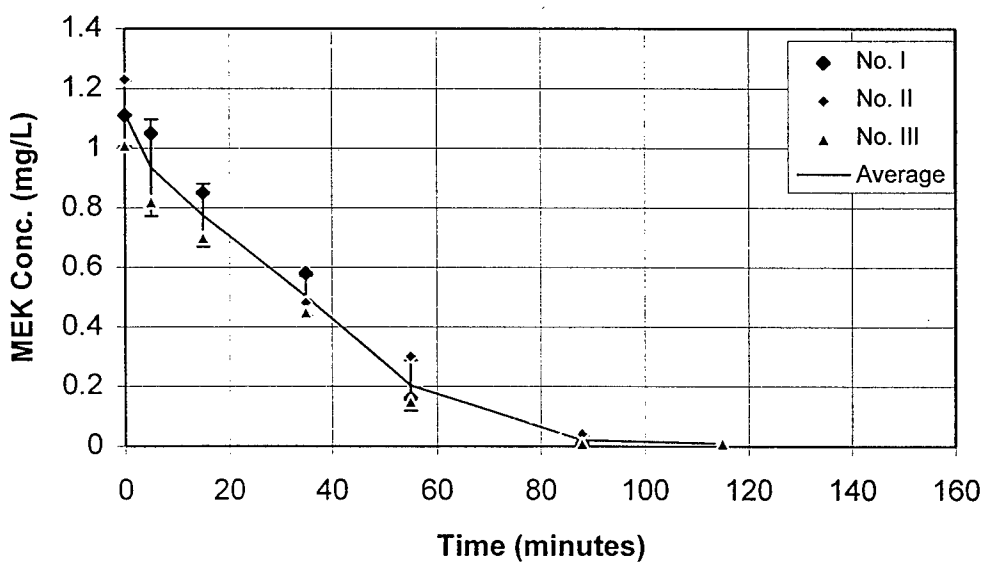
Estimated degradation rate: 2.49×10^{-5} 1/min.

Ketone Kinetic Experiment ---- MEK Degradation Rate in 1/10 Loading

Date: 4/30/96 SS: 0.527 g/L 0.93
Operator: Jing Shi VSS: 0.490 g/L

Time (minutes)	No .I MEK	No. II MEK	No. III MEK	Average	std
0	1.11	1.23	1.01	1.12	0.11
5	1.05		0.82	0.94	0.16
15	0.85		0.7	0.78	0.11
35	0.58	0.48	0.45	0.50	0.07
55	0.16	0.3	0.15	0.20	0.08
88	0.01	0.04	0.01	0.02	0.02
115	0.01	0.01	0.01	0.01	0.00
175					

MEK Degradation Chart



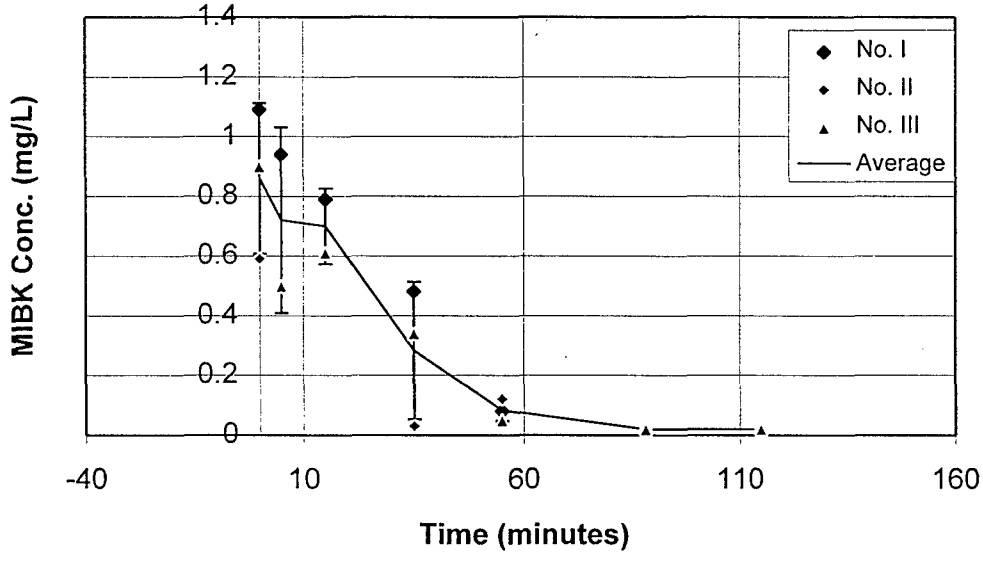
Estimated degradation rate: 2.98×10^{-5} 1/min.

Ketone Kinetic Experiment ---- MIBK Degradation in 1/10 Loading

Date:	4/30/96	SS:	0.527 g/L	0.93
Operator:	Jing Shi	VSS:	0.490 g/L	

Time (minutes)	No. I MIBK	No. II MIBK	No. III MIBK	Average	std
0	1.09	0.59	0.9	0.86	0.25
5	0.94		0.5	0.72	0.31
15	0.79		0.61	0.70	0.13
35	0.48	0.03	0.34	0.28	0.23
55	0.08	0.12	0.05	0.08	0.04
88	0.02	0.02	0.02	0.02	0.00
115	0.02	0.02	0.02	0.02	0.00
175					

MIBK Degradation Chart



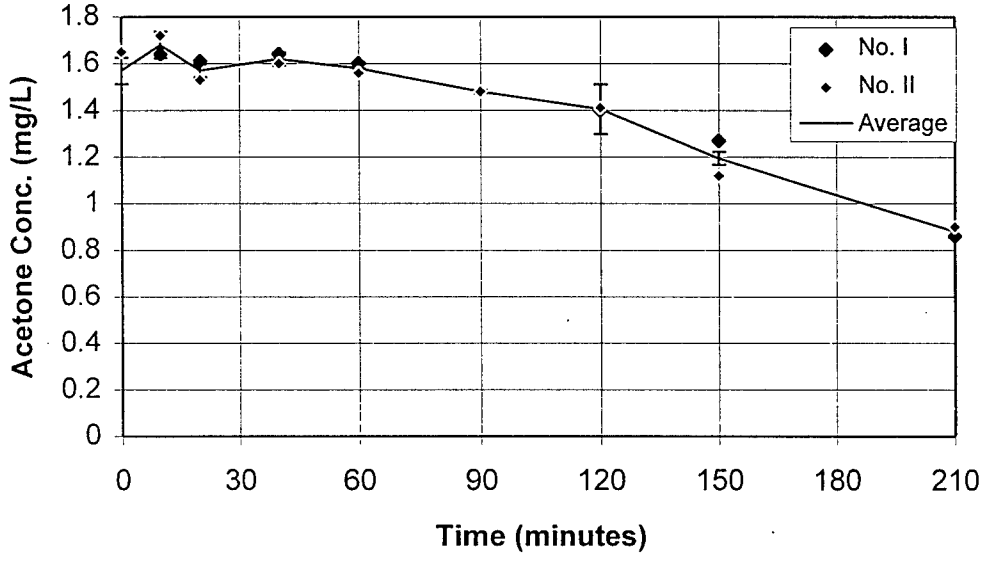
Estimated degradation rate: 3.27×10^{-5} 1/min.

Ketone Kinetic Experiment ---- ACETONE Degradation Rate in 1/100 Loading

Date:	5/23/96	SS:	0.725 g/L	0.93
Operator:	Jing Shi	VSS:	0.672 g/L	

Time (minutes)	No. I Acetone	No. II Acetone	No. III Acetone	Average	std
0	1.49	1.65		1.57	0.11
10	1.64	1.72		1.68	0.06
20	1.61	1.53		1.57	0.06
40	1.64	1.6		1.62	0.03
60	1.6	1.56		1.58	0.03
90	1.48	1.48		1.48	0.00
120	1.4	1.41		1.41	0.01
150	1.27	1.12		1.20	0.11
210	0.86	0.9		0.88	0.03

Acetone Degradation Chart



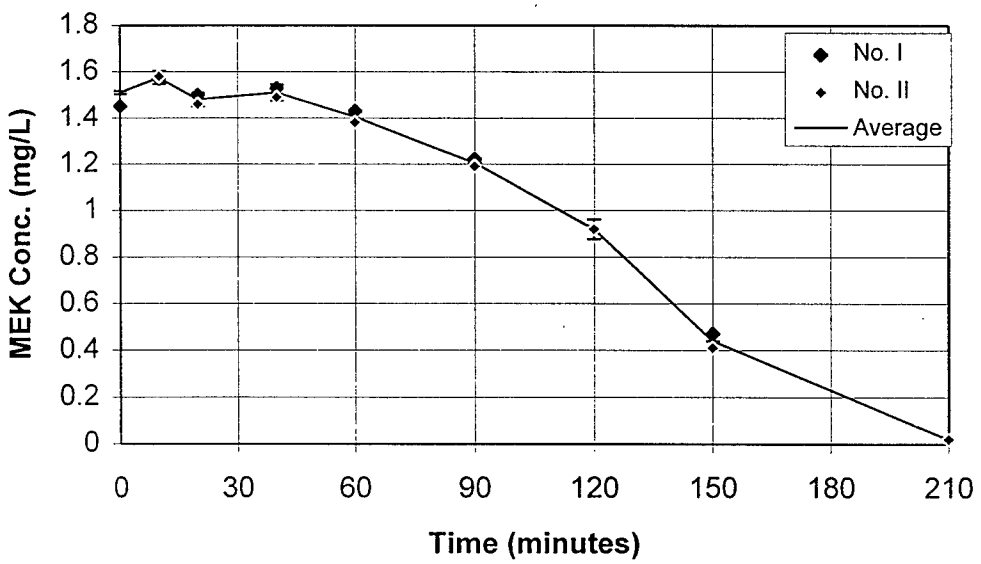
Estimated degradation rate: 0.91×10^{-5} 1/min.

Ketone Kinetic Experiment ---- MEK Degradation Rate in 1/100 Loading

Date: 5/23/96 SS: 0.725 g/L 0.93
Operator: Jing Shi VSS: 0.672 g/L

Time (minutes)	No .I MEK	No. II MEK	No. III MEK	Average	std
0	1.45	1.57		1.51	0.08
10	1.57	1.58		1.58	0.01
20	1.5	1.46		1.48	0.03
40	1.53	1.49		1.51	0.03
60	1.43	1.38		1.41	0.04
90	1.22	1.19		1.21	0.02
120	0.92	0.92		0.92	0.00
150	0.47	0.41		0.44	0.04
210	0.02	0.02		0.02	0.00

MEK Degradation Chart



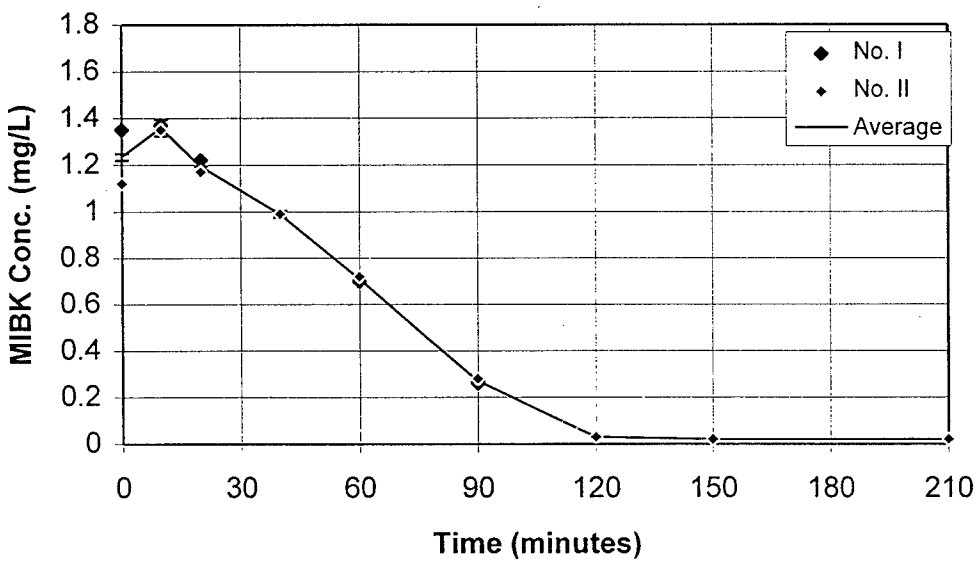
Estimated degradation rate: 1.12×10^{-5} 1/min.

Ketone Kinetic Experiment ---- MIBK Degradation in 1/100 Loading

Date: 5/23/96 SS: 0.725 g/L 0.93
Operator: Jing Shi VSS: 0.672 g/L

Time (minutes)	No. I MIBK	No. II MIBK	No. III MIBK	Average	std
0	1.35	1.12		1.24	0.16
10	1.37	1.35		1.36	0.01
20	1.22	1.17		1.20	0.04
40	0.99	0.99		0.99	0.00
60	0.7	0.72		0.71	0.01
90	0.26	0.28		0.27	0.01
120	0.03	0.03		0.03	0.00
150	0.02	0.02		0.02	0.00
210	0.02	0.02		0.02	0.00

MIBK Degradation Chart



Estimated degradation rate: 2.02×10^{-5} 1/min.

Appendix E

KETONES IN GROUNDWATER

EFX Systems, Inc. **GAC-FBR Design Outline** 16-Aug-96

Influent Characteristics:

Flow, gpm	350.00	Flow, MGD	0.50
Ketones (mg/L)	13.500	Ketone COD (mg/L)	33.1
Acetone	5.000	COD (mg/L)	11.0
MEK	4.000	COD (mg/L)	9.8
MIBK	4.500	COD (mg/L)	12.2
Other COD (mg/L)	10.000	Other COD (mg/L)	10.0
Ammonia-N, mg/l	0.00	NH3-OD, lb/d	0.0
TPH's, mg/l	0.00	TPH COD, lb/d	0.0
Chlorinated, mg/l	0.0	Chlorinated Org OD, lb/d	0.0
Iron, mg/l	1.0	Total COD, mg/l	43.1
Temperature, F	60.0	Total COD, lb/d	180.8
		Total O2 Demand, lb/d	126.6

Fluid Bed Recommendation:

Reactor Diameter:	6	Annual Operating Cost:	$7,429
Quantity:	1	Budget Cost:	$285,000

Fluid Bed Design Parameters:

Actual Design			
Reactor Diameter, ft	6.0	Bed Volume, cf	311
Number of Reactors	1	R+Q Flow, gpm	368
Bed Depth, ft	11	R/Q Ratio	0.1
Flux, gpm/sf	13	HRT, minutes	7
Total COD Load, lb/d/kcf	581		
NH3-OD Load, lb/d/kcf	0		
BTEX-COD Load, lb/d/kcf	149	Carbon, lb ea	4665
NH3 Load, lb/d/kcf	32		
Total O2 Load, lb/d/kcf	407	Carbon Total	4665

Steady State Operating Characteristics:

O2 Used, lb/d	135.0	PSA Size, scfh	79
Effluent O2, mg/l	2.0		
Reactor Influent O2 (mg/l)	30.7		

EFX Systems **GAC-FBR Cost Estimate**

Estimated Operating Costs:

Electric Cost, $KWhr	$0.06	Pump Efficiency, %	78
		Motor Efficiency, %	94
Fluid Pump bhp ea:	10.0	Pump, $/d	$10.74
PBC Pump bhp ea:	0.0	Pump, $/d	$0.00
Growth Control hp	0.5	Pump, $/d	$0.54
Nutrient Feed Pump hp	0.125	Pump, $/d	$0.13
Number of Units	1	Total Pump, $/d	$11.27
Diameter	6.0		
Oxygen PSA, lb/d	135	O2 $/d	$3.64
Standard Nutrients, gal/d	3.7	Nutrients, $/d	$4.83
Attrition, lb/d	0.6	Carbon, $/d	$0.61
		Total, $/d	$20.35
		Total, $/yr	$7,428.54

SECTION 8 - TREATMENT OF PGDN IN BIAZZI NITRATION EFFLUENT UNDER DENITRIFYING (ANOXIC) CONDITIONS AT THE INDIAN HEAD NAVAL SURFACE WARFARE CENTER, INDIAN HEAD, MD

Scale-up and Initial Operation of a Commercial Scale Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) for the Treatment of Propylene Glycol Dinitrate (PGDN) in a Munitions Production Wastewater

Final Report

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September 6, 1996

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EXECUTIVE SUMMARY

During munitions manufacturing, wastewater streams containing nitrated compounds of regulatory concern are generated. A wastewater containing propylene glycol dinitrate (PGDN) and high nitrate concentrations is generated from nitrating propylene glycol (PG) to produce PGDN. The purpose of this project was to evaluate the effectiveness of biological treatment to reduce the concentration of PGDN to below 1 mg/L in the Biazzi plant process effluent water at the Indian Head Naval Surface Warfare Center in Maryland.

The biological fluidized bed reactor (FBR) using granular activated carbon (GAC) as the biomass carrier (GAC-FBR process) was chosen to demonstrate PGDN degradation under denitrifying conditions. The fluidized bed bioreactor is a high rate, biological fixed-film treatment process in which the water to be treated is passed upwards through a bed of fluidized fine-grained media on which microorganisms grow. Biofilms attached to the media remove the organic pollutants from the water. Extensive testing in laboratory scale pilot GAC-FBRs demonstrated PGDN degradation with both PG and EtOH as primary substrates.

A small commercial scale reactor was transported to the Indian Head Division, Naval Surface Warfare Center, erected and hydraulically tested. A feed storage and effluent handling system was set up and connected to the reactor. Several modifications to the FBR system were installed to improve reliability including: a new wastewater feed pump, PG feed pump and holding tank, effluent discharge pump, foam control pump, and in-line water heater. Extensive weather protection and heat tracing were added to the reactor skid and to the influent and effluent systems to permit winter operation.

The reactor was started using a synthetic nitration wastewater. This water had salt concentrations similar to the expected PGDN nitration wastewater. PG was fed as the primary carbon source. The microorganisms used to inoculate the system came from the laboratory scale reactors operated for a previous PGDN degradation project. PGDN was not added to the synthetic feed mixture for material handling safety reasons. To conserve the amount of feed solution needed, each batch of feed was pumped through the reactor 3 to 5 times with constant addition of PG. Batches were discarded when nitrate concentration was exhausted or when concentrations of proteins and ammonia from the breakdown of excess biomass became too high.

A biofilm developed on the GAC rapidly. Mature biofilm coated GAC particles expanded to the growth control point in about three weeks. The reactor was operated and monitored on synthetic feed for five months. During the subsequent five-month period, operation continued with only infrequent feeding and monitoring. Due to mechanical problems with the Biazzi nitration plant, PGDN was not manufactured and wastewater, therefore, was not available for conducting the demonstration.

Several conclusions can, however, be drawn from the start-up and initial operation of this biological GAC-FBR.

- The GAC-FBR unit integrated readily into the established production and treatment train at the Indian Head facility. Safety features provided on the unit were generally adequate to pass the site safety and hazards review.
- Biofilm developed rapidly in the reactor from the microbial inocula provided.
- The reactor operated without problems with the 6% TDS synthetic wastewater containing sodium nitrate and other salts.

- PG was readily degraded and used as an energy and growth substrate under denitrifying conditions by the biofilms that developed on the GAC biomass carrier particles.
- The GAC-FBR proved robust to cessation in feeding of the primary substrate tested, PG. The microbial population in the system was able to quickly degrade PG after intervals of starvation (no substrate feed).
- Because of the high nitrate feed concentration and relatively low COD feed rate (COD:NO_3-N < 4.5:1), some of the nitrate was only partially reduced resulting in some accumulation to nitrite and presumably other reduced intermediates, such as N_2O.
- No pH control was necessary for stable reactor performance. The reactor pH self-regulated between 8.0 and 8.6.

1. INTRODUCTION AND BACKGROUND

During munitions manufacturing, wastewater streams containing nitrated compounds of regulatory concern are generated. At the Indian Head Division, Naval Surface Warfare Center, wastewater containing propylene glycol dinitrate (PGDN) and high nitrate concentrations is generated from production of PGDN in a Biazzi nitration process. The purpose of this project was to evaluate the effectiveness of a small commercial scale biological GAC-FBR reduce the concentration of PGDN to below 1 mg/L in the Biazzi plant process effluent water under production conditions.

The wastewater is produced during final stages of purification after the nitration of propylene glycol with a mixed acid containing concentrated nitric and sulfuric acids. The PGDN is first separated from the spent acid, then purified by a series of carbonate and water washes. The spent carbonate solution and wastewater from these washes are combined into one wastewater stream that is passed through a series of settling tanks to remove any suspended PGDN. The resulting waste stream contains 450 ppm of PGDN on average, 1200 ppm maximum. The concentration of salts may be as high as 6% by weight. The approximate composition of these salts on a dry weight basis is: 70-75% $NaNO_3$, 2-3% Na_2SO_4, 20% Na_2CO_3, 2-3% $NaHCO_3$. The maximum flow rate of the stream is 20 gpm with 7000 gallons a day average total flow.

This wastewater stream has been treated at Indian Head by GAC adsorption of the PGDN. The high nitrate concentration does, however, make this stream a candidate for biological treatment via denitrification. Denitrification is a process where facultative bacteria in the absence of dissolved oxygen and in the presence of nitrate use nitrate as the electron acceptor in place of oxygen. This is termed anoxic conditions. The nitrate is converted (reduced) to molecular nitrogen while

organic carbon is oxidized to carbon dioxide. For this wastewater under anoxic conditions, the PGDN is co-metabolically degraded.

Degradation of PGDN in a laboratory scale pilot FBR was demonstrated as a separate task by MBI and EFX for US Army CERL (MBI/EFX, 1996). The reactor was operated under denitrifying conditions with both PG and EtOH as primary substrates. Effluent PGDN concentrations below the 1 mg/L regulatory limit could be achieved with the system at PGDN loading rates of up to 0.22 Kg COD/m^3-d and overall OLR of 5 Kg COD/m^3-d. PGDN removal rates of greater than 98% were achieved at PGDN loading rates up to 0.89 Kg COD/m^3-d at primary COD/PGDN ratios of 4:1.

1.1 Description of Biological Fluidized Bed Process

The fluidized bed bioreactor is a high rate, biological fixed-film treatment process in which the water to be treated is passed upwards through a bed of fluidized, fine-grained media, such as sand, granular activated carbon or ion exchange resins. Water is passed through the bed at a velocity sufficient to impart motion or fluidization of the media. This occurs when the drag forces caused by the liquid moving past the individual media particles are equal to the net downward force exerted by gravity (buoyant weight of the media). As the water to be treated is passed upwards through the bed of media contiguous films of microorganisms grow (biofilms) attached to the media. This microbial population removes the organic pollutants from the water.

Fluidization of fine grained media allows the entire surface of each individual particle to be colonized by bacteria in the form of a biofilm. Surface areas on the order of 300 m^2/m^3 of bed are common in fluidized bed reactor systems. This results in accumulation of biomass concentrations of up to 50,000 mg VSS/L of

fluidized bed, which is an order of magnitude or greater than the cell mass concentrations obtained in most other biological processes. Fluidization is key to the ability of this process to concentrate active bacterial mass to high levels on small diameter media (<2 mm) without the clogging experienced with packed bed or trickling filters. This superior ability to concentrate active bacterial mass in the reactor has considerable theoretical and kinetic advantages to the performance of the reactor. By manipulating the volume of media added to a system, the fluidization velocity used and the height of the bed is allowed to expand due to biological (biofilm) growth, a great deal of control of the average biofilm thickness and mean cell retention time can be achieved, optimizing overall process performance. The conceptual advantages of biological fluidized bed reactor systems over conventional biological processes include:

- Large surface area for biomass attachment;
- High biomass concentrations;
- Ability to control and optimize biofilm thickness;
- Minimal plugging, channeling or gas hold-up; and,
- High mass transfer properties through maximum contact between biomass and substrate.

In the mid-1980s, it was recognized that the technology may have the potential of substantially reducing the cost of treating groundwater contaminated with industrial wastes. Currently, at thousands of contaminated sites in the U.S., interdiction wells are used to contain VOC pollutants in the subsurface. Water that is pumped from these wells is usually treated with conventional air stripping processes and the effluent air is passed through a granular activated carbon (GAC) module to control VOC emissions. This conventional system of treating interdicted water with 10 ppm or less of VOCs can cost $1-3/1000 gallons, due mainly to the expense for GAC replacement/regeneration. This indicated that the opportunity for

cost reduction lies in the use of biological treatment to destroy most of the pollutant mass instead of loading it on GAC. Yet it was also recognized that a bioprocess that was designed to replace this type of conventional treatment would have to achieve stringent removal capabilities. These included: 1) the ability to remove xenobiotic pollutants (chemicals foreign to biological organisms) at high efficiencies, 2) mobility, 3) the ability to handle a wide range of concentrations and loadings, and 4) resistance to process upsets due to sudden changes in influent concentration and composition. This pointed to the need for implementing the concept of integrating GAC into the biological fluidized bed reactor as the biomass carrier.

The granular activated carbon fluidized bed reactor (GAC-FBR) process is a fluidized bed which employs GAC as the solid support for biofilm growth. The use of an adsorbent carrier offers three advantages. First, essentially complete contaminant removal occurs as soon as the system is commissioned due to adsorption. After rapid development of a mature biofilm, removal is due to biological degradation. Second, the effects of shock loads of pollutants and other perturbations may be buffered by the adsorptive capacity of the GAC resulting in a more stable, robust overall performance. Third, the process provides general removal of a broad range of pollutants whether they are biodegradable or not.

Over the past six years, personnel from EFX Systems, Inc. (EFX), a joint venture company between Ecolotrol, Inc. (Westbury, NY) and MBI International (Lansing, MI), in cooperation with Envirex, Inc., has pursued the application of the GAC-FBR for the cleanup of groundwater contaminated with gasoline, complex wastes and a number of industrial process effluents. Laboratory and field-pilot data in this effort indicated that the GAC-FBR has the capability of removing >99% of the total VOCs from groundwater and process effluents, with high removals of semi-volatile compounds as well. Full-scale systems are now operation at field sites with flow rates as high as 4,000 gpm (5.8 million gallons/day).

2. RATIONALE AND PLAN

Wastewater from the PGDN production process is generated in batches of about 7000 gallons per day at a PGDN concentration of about 450 mg/L. Based on the results obtained during the laboratory scale tests, a volume of around 300 gal/day could be applied to the reactor at loading rates commensurate with consistently achieving effluent PGDN concentrations below the regulatory limit of 1 mg/L. Therefore, plans for this demonstration called for collection of a representative volume of this water for storage and subsequent feeding of the wastewater to the GAC-FBR for treatment. Indian Head personnel anticipated approximately two production runs of PGDN and, therefore, two batches of wastewater available for treatment during the course of the demonstration.

Because volume of wastewater was limited, provision was made to make synthetic feed to grow a mature biofilm on the GAC prior to feeding the actual wastewater. This would allow using all PGDN contaminated wastewater to test reactor performance. The synthetic feed would also allow maintenance of the reactor between production runs. Concentrations of sodium nitrate and other salts in the synthetic feed were calculated to match anticipated concentrations in the real wastewater. Due to safety considerations, PGDN could not be incorporated into the synthetic feed. To conserve the synthetic feed and fully utilize the nitrate (electron acceptor), provision was made to recycle the feed through the reactor three to five times or until the nitrate concentration was depleted. Because it was readily available on site, PG was selected for use as the primary carbon source.

Initial project plans called for a three to four month test program with about 75% of the program devoted to treating actual wastewater. A four to six week period of biological start-up using the synthetic feed was designated as the first task. The reactor was to be maintained on synthetic feed until wastewater became

available. The second task was to demonstrate PGDN removal at a loading rate found to achieve PGDN effluent concentrations below the regulatory limit of 1 mg/L. The third task was to test one or two additional (higher) applied loading rates with wastewater from the second production run. The sampling plan concentrated on collecting data during periods when the reactor was fed actual wastewater. Daily sampling and analysis of PGDN and two to three times per week sampling of PG and NO_3-N was proposed.

Discharge permits at the site demanded that the biologically treated wastewater be polished using GAC absorption. Therefore, effluent tanks and bag filters (to remove biosolids), an effluent/transfer pump and transfer piping network were installed. Initial plans called for executing the treatment demonstration during the summer and fall to avoid any requirements for freeze protection of the reactor and other treatment system components. However, suspension of the PGDN production schedule due to mechanical problems early in the start-up phase resulted in a delay of the original schedule. As a result, incorporation of freeze protection into the project plan was required.

3. MUNITIONS WASTEWATER TREATMENT SYSTEM

3.1 Biological Fluidized Bed Reactor

An Envirex Model 30 fluidized bed reactor was installed for this treatment demonstration (Figure 3-1). This reactor was assembled to specifications from MBI/EFX Systems for a CERL sponsored project at the Radford Army Ammunition Plant. The reactor shell is 20 inches in diameter, 16 feet tall and has a 0.71 m^3 working volume. The reactor has provision for operating under aerobic, anoxic and anaerobic conditions. A programmable logic controller is used to monitor the system instrumentation, control temperature and pH, and execute interlocks.

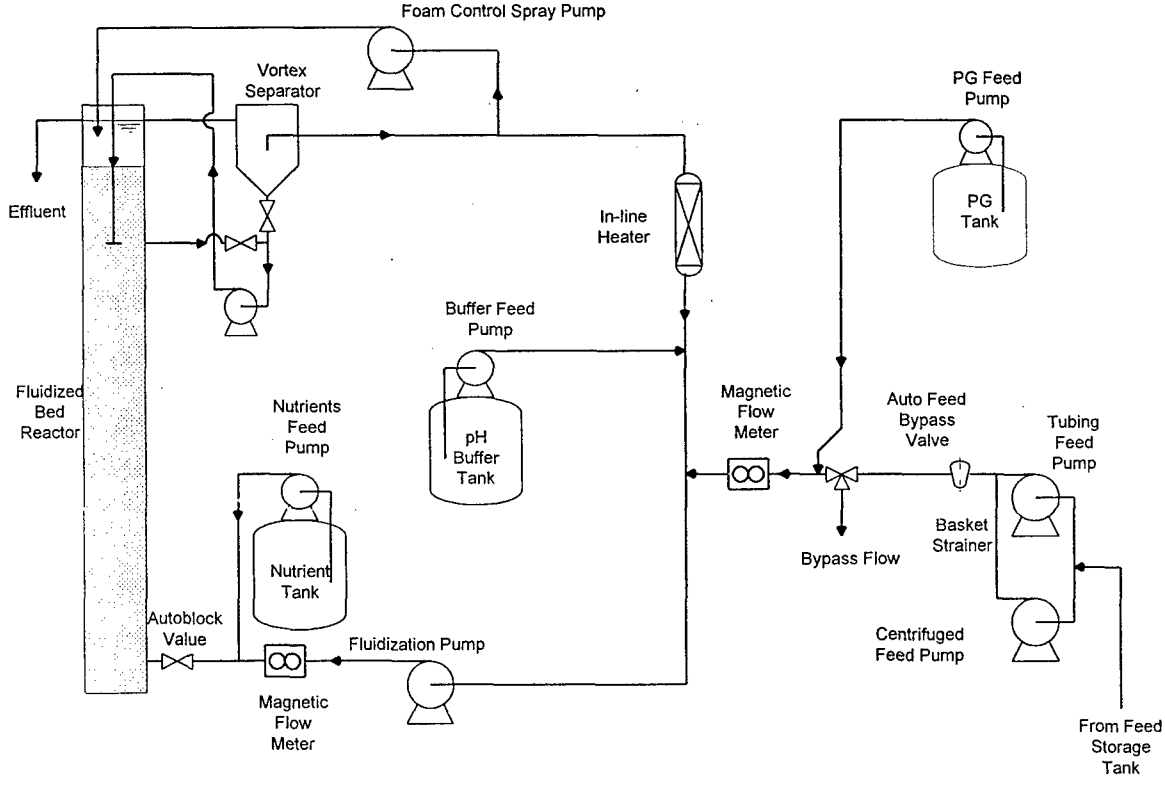

Figure 3-1. Simplified Schematic of GAC-FBR used at the Indian Head Site

The fluidization flow enters the reactor through four distribution cones arranged about one foot above the base plate. The target fluidization flow rate is 30 to 36 gpm which gives a flux rate of 12 to 14 gpm/ft^2. Water travels up the reactor fluidizing the media and exits the reactor through a 4 inch diameter pipe. The water flows to a vortex separator where any media, buoyed from the system due to attached gas bubbles, is separated from the liquid stream. From the separator, a portion of the water returns by gravity through recycle piping to the fluidization pumps and is pumped back through the reactor. Effluent water overflows the reactor through a 2 inch effluent pipe.

Influent water is pumped into the system using a feed pump that discharges to the suction side of the fluidization pump. Thus, a constant flux rate in the reactor is maintained regardless of the influent flow rate. Nutrients (phosphate and ammonia), primary substrate (PG), and pH control chemicals are pumped into the recycle line by separate metering pumps. Other features and components of the biological GAC-FBR are detailed in Table 3-1. In addition, several improvements, modifications and repairs to the reactor system were made after the reactor arrived at Indian Head (Table 3-2). These changes improved the reliability of the system, especially for pH, temperature and influent flow rate control.

3.2 Influent and Effluent - Feed and Storage Equipment

Tanks with associated piping and valves were installed at the site to store and handle the influent and effluent (Table 3-3, Figure 3-2). The five, 1400-gallon dome top polyethylene, tanks were sized to hold the water from one day of PGDN production, the day when PGDN concentrations were likely to be highest. The tanks fill one at a time as the operator opens the filling valves on the manifold above the tanks. Each tank is fed to the reactor by opening the valve to the feed manifold at the base of the reactor. Effluent from the bioreactor can be directed to either of two

additional 1400-gallon dome top polyethylene effluent tanks from the effluent manifold piping and valving. All pipes are PVC.

Table 3-1. Fluidized Bed Reactor Components

Component	Purpose
Reactor shell	Holds media with attached biomass and fluid distribution system
Vortex separator	Captures and media that float up in the reactor from attached gas bubbles
Fluidization pump	Provided the fluidization flow to the base of the reactor
Feed Pump	Provides wastewater forward feed to the system
PG feed tank and metering pump	Provides regulated flow of primary substrate to the system
Nutrient feed tank and metering pump	Provides a regulated flow of mineral nutrients (phosphate and ammonia) to the system
pH buffer tank and metering pump and pH probes	Provide a regulated flow of acid or base to control the pH of the wastewater
Media return/ biomass control pump	Pumps media captured by the separator back into the reactor and controls the bed height by pumping media from the bed and gently shearing off some biofilm
Foam control pump	Provides a spray of effluent water at the top of the reactor to suppress foam from biological gas production
In- line Heater and temperature probe	Controls reactor temperature at the desired above ambient temperature
Reactor shell insulation	Insulation blankets for reactor shell and separator installed to reduce heat loss
Magnetic flow meters	Monitor the flow rate of feed and recycle
Basket strainer	Strain any large particles from the feed stream to protect pumps and the distribution system from clogging
Feed bypass valve	Shuts off or diverts feed from system under certain interlocked conditions
Reactor block valve	Shuts off reactor flow to prevent media from backflowing into the distribution system under interlocked shut down
Air compressor	Provides compressed air to actuate automatic valves and to supply oxygenation equipment
Oxygenation Equipment	Not used for anoxic treatment on this project
Oxygen generator	Generates oxygen by pressure swing adsorption for providing electron donor to aerobic systems
Metering valve, DO probes, and PID controller	Control dissolved oxygen concentration at desired level by feed back control from probes to valve
Venturi injector	Provides high shear mixing and dissolution of oxygen into water
Bubble trap	Disengages oxygen bubbles the recycle stream so that no undissolved gas reaches the fluidized bed
Electrical control panel	Provides power distribution and switching to all equipment and instrumentation
Programmable logic controller	Controls the process and system alarms and interlocks
Operator interface screen	Displays flows, temperature, pH and alarm status and provides menu for changing system set points

Table 3-2. Improvements, Modifications and Repairs to Reactor and Equipment Skid

Equipment	Purpose
Propylene glycol storage tank and metering pump	One 25 gal tank and diaphragm pump installed to dispense the carbon source
Secondary containment	One 25 gal tank each for the propylene glycol and HCl pH adjusting solution tanks to prevent spills
Centrifugal feed pump	Installed to replace unreliable original equipment, for feed rates of 0.5 gpm or more
Feed control valve	Diaphragm valve (1 inch) installed to control flows better at low flow rates
Peristaltic tubing feed pump	Installed for low feed rates of 0.5 gpm or less
Feed pump secondary containment and leak detection	Leak containment container with level switch to turn of pump in the event of split pump tubing
Foam control pump	Magnetically coupled centrifugal pump (8 gpm max) installed to replace undersized original for water spray foam suppression
Foam suppression system	Low flow pump and timer added to dispense vegetable oil as a foam suppression agent
Effluent line	Effluent line from separator blinded off and a new effluent line from the main reactor shell installed, for facilitating effluent tank access and freeze protection
Media return/ biomass control pump	Replaced all seals and gaskets
In- line Heater	Installed in recycle line with by-pass valves to keep process at desired level
Reactor shell insulation	Insulation blankets for reactor shell and separator installed to reduce heat loss
Interlocks and controls	
Operator interface screen	Defective screen replaced with a new unit
Effluent pump	Switch provided installed to start and stop effluent pump
Propylene glycol metering pump	Interlocked to the same logic as the nutrient addition pump to correctly respond to shut down conditions
Feed pump	Interlocked to the same logic as the three way feed control valve to correctly respond to shut-down conditions
Ladder logic program	Various modifications to improve flexibility including addition of two sided pH control and reset criteria for temperature and pH
Interlock table	Document rewritten to show changes in interlocks and ladder logic

An effluent pump was installed to pump the effluent from the two effluent tanks to the activated carbon absorbers in Building 1695. These GAC absorbers are the current system for PGDN wastewater treatment at Indian Head. This polishing step was required in the permitting of this demonstration. Bag filters (20 µm) are used to remove excess biosolids from the effluent to prevent clogging of the carbon absorbers.

Table 3-3. Feed and Effluent Storage and Handling Equipment Installed	
Equipment	Purpose
Feed storage tanks	5x 1400 gal tanks for storing the PGDN contaminated water from a single production run
Effluent tank	2x 1400 gal tanks for holding effluent until it can be sent to the GAC adsorbed polishing unit
Effluent/ transfer pump	Dual purpose pump supplied and controlled from the skid to pump effluent to the carbon polish unit or transfer effluent to an empty feed tank
Bag filters	Two units plumbed in parallel with a flow control diaphragm valve to remove biosolids from the effluent before the effluent passes the GAC absorbers
Feed and effluent piping and valving	Network of piping and valves for flexible transfer of water between feed and effluent tanks
Electrical service and grounding	480 volt service for skid and heat tracing transformer, grounding of skid, reactor, effluent pump, and bag filters for lightning protection
Eye wash and first aid kit	Portable safety station to serve the skid and tank area
Telephone hook-up with answering machine	Located in an adjacent building to facilitate communication between personnel at Indian Head and at EFX
Weather proofing	For freeze protection during winter weather
Skid enclosure	Plywood panels installed to protect skid piping
Transformer and heat tracing	Transformer installed on skid supplying heat tracing tape to the feed and effluent piping and valving
Tarp enclosure for tanks	Tanks covered for freeze protection
Steam heaters for tank and skid enclosures	Low level heat source to prevent freeze up of feed and effluent

3.3 Freeze Protection

Delays in the production schedule due to mechanical and contractor problems with Biazzi plant pushed the time schedule for the demonstration into the winter months. Therefore, provisions were made for weatherproofing and freeze protecting the equipment during cold weather operation (see Tables 3-2 and 3-3). Considerable resources were expended to enclose the bioreactor equipment skid and cover the tanks with tarps. Steam heaters were installed in the skid and tank enclosures and feed and effluent lines were electrically heat traced. Insulation blankets and an in-line heater were installed on the bioreactor.

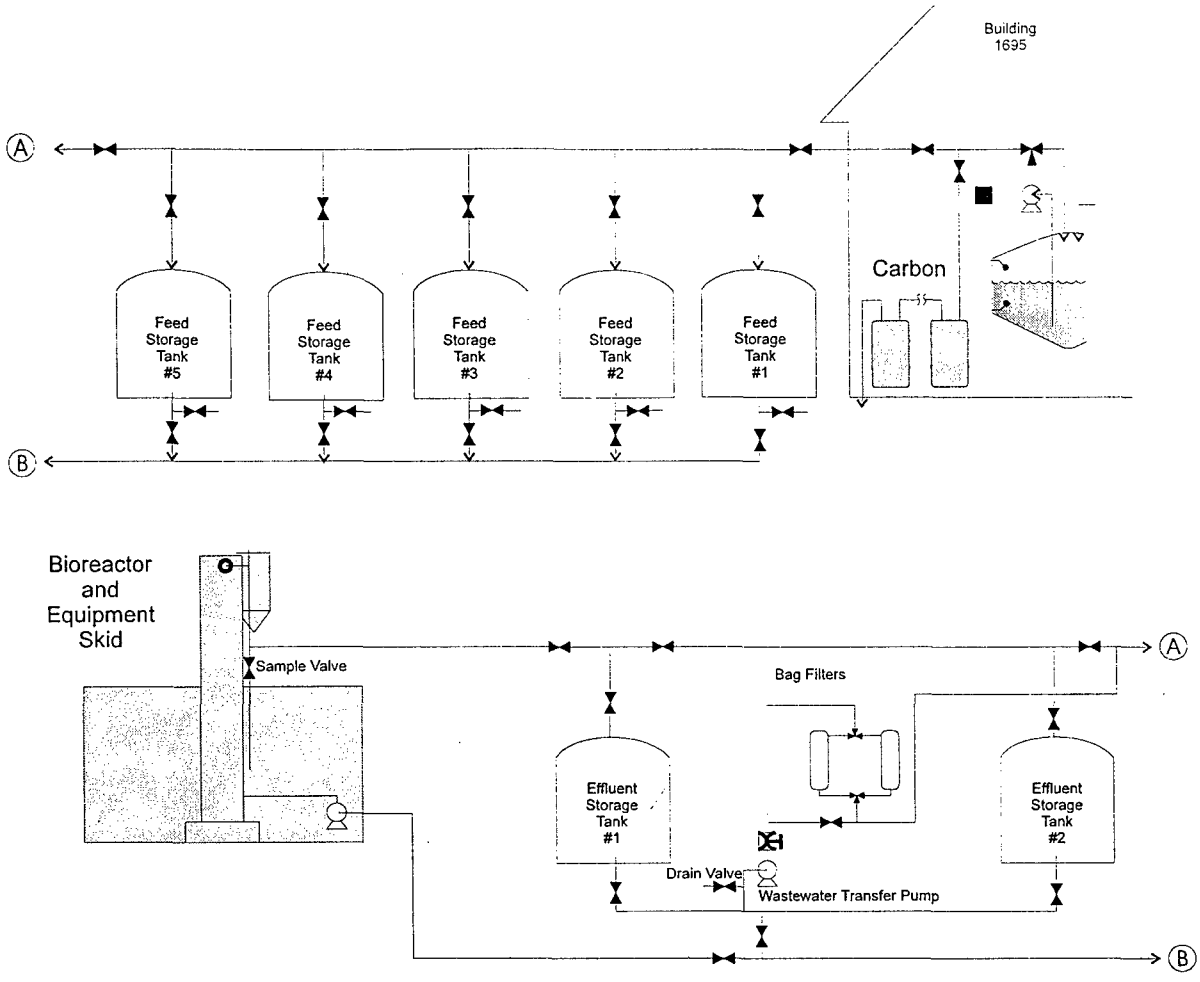

Figure 3-2. Wastewater Feed and Effluent Storage and Handling System at the Indian Head Site

3.4 Assembly and Hydraulic Testing

The reactor was disassembled and packed up at the Radford Army Ammunition Plant and shipped to Indian Head on 24 August 1995. The reactor was assembled on 18-20 September 1995. The feed and effluent handling systems were installed during late September and early October. EFX Systems, Inc. took primary responsibility for assembly of the reactor. Indian Head personnel took primary responsibility for installing the feed and effluent handling systems. Greg Wilson from the University of Cincinnati assisted in reactor installation.

The reactor was filled with plant process water and all piping and valves checked for leaks. Tanks, valves and piping in the feed and effluent system were tested by filling one tank and then transferring the water from tank to tank with the effluent/transfer pump.

Four, 55-lb bags of GAC (Calgon MRX- P, 10 x 30 mesh) were added to the reactor. The GAC was fluidized and about four inches of carbon fines were siphoned from the top of the fluidized bed.

3.5 Feed Preparation

Synthetic wastewater feed (6% TDS) was prepared in one of the 1400-gallon feed tanks using the salts listed in Table 3-4. The components were chosen to match the nitrate and salt concentrations in the PGDN production wastewater. The feed tank was filled approximately 1/3 full with plant process water, the bags of salts were dumped directly into the tank, and the tank was topped off. The transfer pump was operated (drawing from tank bottom, discharging at tank top) to thoroughly mix the solution and dissolve the added salts. Six batches of feed were prepared over the course of the project The amounts of sodium carbonate, sodium bicarbonate and nitric acid were adjusted to obtain the desired pH. Due to safety considerations, PGDN could not be incorporated into the synthetic feed.

Technical grade propylene glycol, used in PGDN manufacturing at Indian Head, was used as the carbon source for the bioreactor. The material was placed in a 25 gallon polyethylene feed tank and pumped directly to the bioreactor. To decrease the viscosity during cold weather, the PG was diluted to a 50% solution in the feed tank. The PG metering pump was set to achieve the desired applied organic loading rate (OLR). The COD value of PG is 1.68 g COD/g PG.

Table 3-4. Composition and Date of Preparation of Synthetic Wastewater						
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6
Date prepared	11/6/95	12/15/95	1/26/96	2/23/96	3/25/96	4/15/96
Na_2CO_3 (lb)	150	0	0	0	0	0
$NaHCO_3$ (lb)	25	100	100	100	50	0
$NaNO_3$ (lb)	600	600	500	500	600	600
Na_2SO_4 (lb)	50	50	50	50	50	50
Total (lb)	825	750	650	650	700	650
TDS (%)	7.1%	6.4%	5.6%	5.6%	6.0%	5.6%
Initial NO_3-N Conc. (mg/L)	8500	8500	7100	7100	8500	8500
NO_3-N Conc. when Discarded (mg/L)	840	180	860	710		
Note: nominal fill volume of tank was 1400 gallons.						

Nutrient solution was prepared by mixing a 9 lb. bag of Bionutrients 36 into 25 gal of water in a polyethylene feed tank. Bionutrients 36 is a dry salt mixture of 6 lb. urea and 3 lb. ammonium phosphate. The nutrient metering pump was set to give a COD:N:P ratio of 100:5:1. For about three weeks, ammonia nitrogen input was reduced by replacing 60% to 100% of the Bionutrients 36 with sodium phosphate monobasic.

A buffer solution for pH control was prepared from HCl (1.5 N) in a 25 gal polyethylene feed tank. The pH control system was rarely operated during the demonstration. The minor adjustments made to the synthetic feed were adequate to ensure the pH did not exceed 9.0.

4. OPERATION AND MAINTENANCE OF THE BIOREACTOR

4.1 Biological Start-up

Biological start-up commenced immediately after hydraulic testing was completed. Biomass for inoculation of the system was collected from the pilot-scale GAC-FBR operated by MBI/EFX for the initial treatability testing of PGDN degradation. Two batches of biofilm-coated GAC were added: 3 liters of GAC with mature biofilm harvested from the laboratory pilot FBR, and 20 gallons of GAC with a limited amount of attached biomass which had been settled out of the laboratory-pilot effluent stream.

On 3 November 1995, the FBR was filled with the synthetic wastewater. The GAC with biomass was added to the top of the reactor and the reactor placed on 100% recirculation overnight to encourage the microorganisms to attach to the GAC. Feed of the synthetic wastewater, PG and nutrients began the next day. Initial conditions were: PG loading of 5.3 kg COD/m^3-d , synthetic wastewater flow rate of 0.95 L/min, fluidization flow rate of 30 gpm, fluidized bed height was 7.9 feet, reactor pH was ca. 8.3 and reactor temperature was 16°C. Nitrogen gas bubbles and foam appeared in the reactor within one week of inoculation.

4.2 Bioreactor Operation and Maintenance with Constant Feeding

The conditions established for start-up were maintained, with only minor changes, for the next six months (Figures 4-1 and 4-2). The temperature during this period ranged between 10 and 38°C, but was generally controlled at about 30°C. The pH self regulated at about 8.6 with a range of 7.9 to 9.2. The influent water pH was occasionally adjusted with nitric acid since the denitrification reaction generates alkalinity.

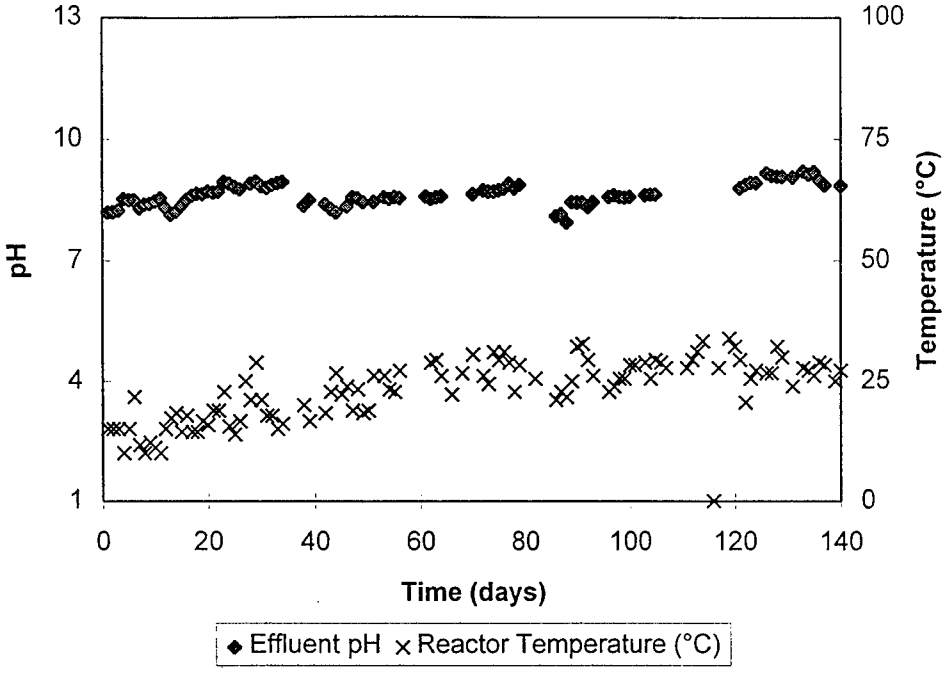

Figure 4-1. Effluent pH and Temperature for a Small Commercial Scale GAC-FBR Treating synthetic Munitions Production Wastewater

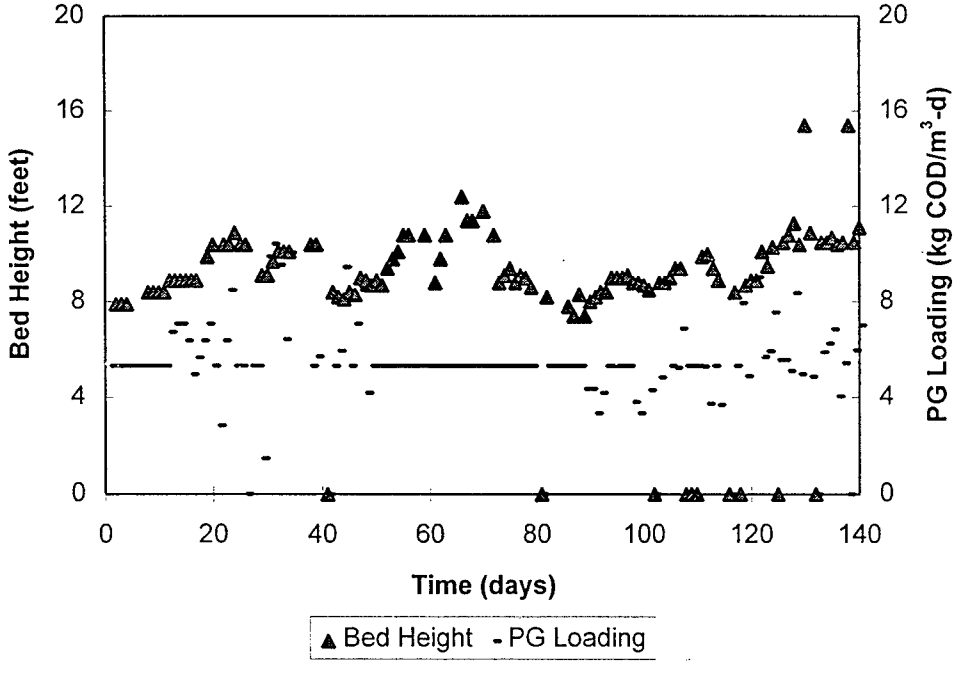

Figure 4-2. Organic Loading Rate and Fluidized Bed Height for a Small Commercial Scale GAC-FBR Treating Synthetic Munitions Production Wastewater

The bed height increased over the first three weeks reaching a steady level at about 10.4 feet. Attaining a steady bed height marked the end of the start-up period (Table 4-1). The rate of bed growth in this reactor was typical for a denitrification system operated at an applied OLR of 5 kg COD/m^3-d. The relatively steady bed height represents a balance between biofilm growth and shearing from induced by the production of gas (N_2) within the system.

Table 4-1. Summary of Operational Periods of the Anoxic GAC-FBR at Indian Head NSWC

Dates	Day	Period	Feed Regime
11/6 to 11/27	0 to 21	Start-up	Constant feed of nitrate and PG
11/28 to 4/23	22 to 168	Constant feed maintenance	Constant feed of nitrate and PG
4/24 to 6/9	169 to 215	Intermittent feed maintenance	Two hours per week feed of nitrate and PG
6/10 to 8/30	215 to 297	Stand-by	Recycle operation only, no feed

Six batches of feed were prepared and fed to the reactor during the course of the demonstration period (Table 3-4). Each tank of synthetic wastewater was passed through the reactor several times in order to fully utilize the initially high concentrations of nitrate. The final nitrate concentrations of four feed batches are shown in Table 3-4; some intermediate feed and nitrate values are shown in Table 4-2. It is quite clear from the data that nitrate was reduced on each pass through the bioreactor.

4.3 Consequences of Reusing the Synthetic Wastewater Feed

PG was continuously supplied to the reactor. The excess biomass produced was sheared from the GAC carrier particles and wasted in the effluent from the system. Nitrate was always present in excess (COD:NO_3-N<4.5) so that the PG added was essentially completely removed. Typically, the nominal PG feed concentration of 1730 mg/L was reduced to 20 mg/L or less. Most of the biomass was filtered out of the feed water using a 20 µm filter bag before the wastewater was

reused for another pass. However, some degradation of the excess biomass occurred in the effluent holding tank between uses releasing cellular breakdown products. Water used for 30 days or more acquired a very strong ammonia odor. The high pH in the reactor tended to push the ammonium-ammonia equilibrium toward unionized ammonia.

Table 4-2. Changes in Nitrate and Nitrite Concentration of Synthetic Wastewater as it was Reused.

	Nitrate (mg/L as N)		Nitrite (mg/L as N)		
Date	Influent	Effluent	Influent	Effluent	Theoretical Use of COD (mg/L)*
1/28	6809	6222	38	223	1490
1/29	5912	4935	130	230	3250
2/8	4694	3185	810	1107	4460
2/21	1373	401	1260	1313	3400
2/23	856	12	1250	833	4070

Influent PG concentration was 1730 mg/L (2900 mg COD/L)
Flow rate = 1.0 L/min
OLR = 5 kg COD/m^3-d

*Assumes
3.7 mg COD/mg NO_3^--N reduced to N_2
2.3 mg COD/mg NO_2^--N reduced to N_2
1.41 mg COD/mg NO_3^--N reduced to NO_2^--N
(McCarty, P. L. et al., Biological Denitrification of Wastewaters by Addition of Organic Materials, Proc. 24th Purdue Indust. Waste Conf., pp. 1270-1285, 1969)

Reuse of the feed and the subsequent build-up of ammonium and soluble protein caused several operational problems. First, nitrogen gas production decreased and some biofilm sloughing occurred when the water began to have a strong ammonia-type odor. The decrease in bed height is shown in Figure 4-2. Second, proteins in the water from decayed cells resulted in considerable foam production at the top of the reactor. This foam could not be suppressed with a vigorous water spray of about 2 gpm. Vegetable oil was added as a foam suppresser for this condition. Biofilms recovered quickly (Figure 4-2) and foam production diminished when new synthetic wastewater was prepared.

4.4 Nitrite in the Treated Effluent

Under normal conditions, anoxic treatment systems are operated with sufficient electron donor (substrates) to completely reduce the amount of nitrate in the water since the purpose of denitrification systems in wastewater treatment is for removing nitrates, in general. That is not the case in the cometabolic degradation of PGDN in the nitration process effluent. The objective here is to provide sufficient substrate to ensure the PGDN concentration is reduced to less than 1 mg/L in the treated effluent. As a result, the ratio of COD:NO_3-N was well below the 4.5:1 ratio generally used. As a result of this, some accumulation of nitrite was observed in the treated effluent. Typical results of the gradual decrease in nitrate and increase in nitrite in the water as it was reused are presented in Table 4-2.

The amount of COD added is less than that calculated to provide reduction of the nitrite and nitrite to N_2 (Table 4-2). It is likely that accumulation of other partially reduced intermediates, such as N_2O also occurred. Use of some of the soluble products from lysis of the excess biomass could have contributed to the COD available for denitrification as well.

4.5 Reactor Operation Under Intermittent Feed and Standby Conditions

Because of continuing delays in PGDN production, the bioreactor was placed into an intermittent feeding mode for six weeks beginning on 24 May 1996 (Table 4-1). For about two hours each week synthetic feed was pumped to the reactor and PG and nutrients applied. Gas production was evident during the feeding session. Occasional flushing with fresh feed seemed to reduce the build up of ammonia odors and proteins in the water. Little maintenance was required during this time.

Beginning on 30 August, the reactor was placed in standby mode. The reactor media was kept fluidized by the recirculation pump but no synthetic feed or PG was applied. These conditions were maintained up to the time of this report (about 12 weeks). Laboratory reactor tests have shown that biomass remains attached to the media and is capable of degrading PG after up to three weeks in standby conditions.